1912

The Petroleum System—Status of Research and Methods, 1990

U.S. GEOLOGICAL SURVEY BULLETIN 1912

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Petroleum System Definition and Classification Scheme

A petroleum system encompasses a hydrocarbon source rock and all generated oil and gas accumulations and includes all the geologic elements and processes that are essential if an oil and gas deposit is to exist. **Petroleum** includes concentrated occurrences of any of the following substances: thermal and microbial natural gas found in conventional reservoirs as well as in gas hydrate, tight sandstone, fractured shale, and coal; and condensates, crude oils, heavy oils, and solid bitumen found in reservoirs in siliciclastic and carbonate rocks. **System** describes the interdependent geologic elements that create oil and gas accumulations. These elements include a petroleum source rock, migration path, reservoir rock, seal, and trap; and the geologic processes that create each of these basic elements. All these elements must be correctly placed in time and space so that organic matter included in a source rock can be converted into a petroleum deposit. A petroleum system exists wherever all the basic elements are known to occur or are thought to occur.

Characteristics and Limits.—The stratigraphic, areal, and temporal extent of the petroleum system is specific. Stratigraphically, the system includes the following rock units: a petroleum source rock, rocks through which migration has occurred, a sealed reservoir rock (trap), and the rock overburden (time and temperature) required for maturity. The areal extent of the petroleum system is defined by a line that circumscribes the mature source rock and all oil and gas deposits, conventional and unconventional, originating from that source. Since microbial gas originates from immature source rocks, the gas deposits themselves or the geologic setting defines the extent of the system.

The events of a petroleum system are defined by two periods of geologic time, the duration time and the preservation time. The duration is the time required to form a petroleum system. If the source rock is the first or oldest unit deposited and the overburden necessary to mature the source rock is the last or youngest element, then the age difference between the oldest and youngest element is the duration of the petroleum system. For example, a Devonian source rock (380–390 Ma) is buried by Pennsylvanian and Permian rocks (250–290 Ma) to maximum depth in the Late Permian(250 Ma); expulsion (primary migration) of hydrocarbons occurs during the Permian (250–275 Ma). These hydrocarbons migrate (secondary) and accumulate in reservoirs of Pennsylvanian age (300–315 Ma) and in traps that formed in the Late Pennsylvanian and Early Permian time (270–290 Ma). The duration of this petroleum system is 140 million years.

Preservation time starts after migration (secondary) and accumulation are complete. If little or no tectonic activity occurs during the preservation time, accumulations will remain in their original position. Remigration (tertiary) happens during the preservation time if folding, faulting, uplift, or erosion occur. If all accumulations are destroyed during the preservation time, no record of the petroleum system will be left. In the example, the preservation time is 250 million years.

Level of Certainty.—A petroleum system can be identified at three levels of certainty: **known**, **hypothetical**, and **speculative**.The level of certainty indicates the confidence for which a particular source rock has generated the hydrocarbons in an accumulation. In a **known** petroleum system, in the case of oil, a good geochemical match exists between the source rock and the oil accumulations; or, in the case of natural gas, the gas is produced from a gas source rock. In a **hypothetical** petroleum system, geochemical information identifies a source rock, but no geochemical match exists between the source rock and the petroleum deposits. In a **speculative** petroleum system, the existence of source rocks and petroleum accumulations is postulated entirely on the basis of geologic or geophysical evidence. At the end of the system's name, the level of certainty is indicated by (!) for **known**, (.) for **hypothetical**, and (?) for **speculative**.

Petroleum System Name—The name of the petroleum system includes the source rock, followed by the name of the major reservoir rock, and then the symbol expressing the level of certainty. For example, the Torok-Nanushuk(.) is a **hypothetical** system on the North Slope of Alaska consisting of the Cretaceous Torok Formation as the source rock and the Nanushuk Group sandstone as the major reservoir rock.

Classification Scheme.—A petroleum system can be classified into one of 12 categories, based on the type of source rock (I, II, or III; Tissot and Welte, 1984, p. 512), the composition of the reservoir rock(siliciclastic or carbonate), and whether the system is purebred or hybrid. A purebred petroleum system was deposited in a geologic setting in which the structural framework did not change significantly during the geologic life of the system; in contrast, a hybrid system includes a major structural change, without which a petroleum system would not have formed. The composition of the reservoir rock refers to the lithology of the largest petroleum deposit, whether it is siliciclastic or carbonate. The organic-matter type may be I, II, or III and is distinguished on the basis of the hydrogen and oxygen indices of the kerogen when plotted on the van Krevelen diagram (Tissot and Welte, 1984). The organic-matter type that produced the petroleum in the largest petroleum deposit is used to classify the system. The largest petroleum deposit refers to a single pool that contains the most in-place hydrocarbons, or a series of pools that cumulatively contain the most in-place hydrocarbons in the system at the time of discovery.

Reference Cited.—Tissot, B.P., and Welte, D.H., 1984, Petroleum formation and occurrence: New York, Springer-Verlag, 699 p.

The Petroleum System—Status of Research and Methods, 1990

LESLIE B. MAGOON, Editor

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The Petroleum System—Status of Research and Methods, 1990

Abstract

Leslie B. Magoon, *Editor*

This publication in 17 individually authored summaries by U.S. Geological Survey scientists presents a revised and expanded list of the petroleum systems within the United States and summarizes the status of research for a number of petroleum-related topics and investigative methods. The revised and expanded list now includes 130 petroleums systems within the United States, 25 of which are classified as *known* systems.

In a brief description of the usefulness of the stratigraphic cross section, Molenaar shows how this type of graphic illustration depicts important vertical and lateral lithostratigraphic relations. Two summaries on ancient and modern deep-water sediments are included. The carbonate slope apron and base-of-slope apron are compared and contrasted by Cook and Mullins. Summarizing the work of many investigators, Normark indicates how siliciclastic fan models based on field mapping, submarine acoustic imaging, and subsurface seismic stratigraphy compare and contrast. Investigations about porosity in petroleum reservoir rocks are discussed by Schmoker and Gautier. Pollastro discusses the uses of clay minerals as exploration tools that help to elucidate basin, source-rock, and reservoir history. The status of fission-track analysis, which is useful for determining the thermal and depositional history of deeply buried sedimentary rocks, is outlined by Naeser. The various ways workers have attempted to determine accurate ancient and present-day subsurface temperatures are summarized with numerous references by Barker. Clayton covers three topics: (1) the role of kinetic modeling in petroleum exploration, (2) biological markers as an indicator of depositional environment of source rocks and composition of crude oils, and (3) geochemistry of sulfur in source rocks and petroleum. Anders and Hite evaluate the current status of evaporite deposits as a source for crude oil.The current knowledge on the effect of biodegradation on crude oils is covered by Michael. Research on the origin and recovery of heavy oil and natural bitumen is discussed by Meyer. Two contributions on gaseous hydrocarbons are included: Kvenvolden discusses the latest thinking on the origin of methane and nitrogen, redefines the terms associated with the origin of methane, and suggests possible implications these ideas have on exploration strategy; and Collett and Kvenvolden review investigations of marine and continental natural gas hydrate occurrences. Crovelli reviews quantitative aspects of petroleum resource assessment methodologies. Lastly, publications written by personnel of the USGS Branch of Petroleum Geology and published during 1988 are listed in a separate bibliography.

Manuscript approved for publication, September 26, 1989.

Identified Petroleum Systems within the United States—1990

By Leslie B. Magoon[1]

INTRODUCTION

Basin analysis, petroleum system, play, and prospect may be viewed as separate levels of investigation, all of which are needed to better understand the genesis and habitat of hydrocarbons. Basin analysis emphasizes structural depressions and the included sedimentary rocks, the petroleum system emphasizes the genetic relation between a source rock and an accumulation, the play emphasizes structural and stratigraphic reservoir trends, and the prospect emphasizes individual traps. Except for the petroleum system, these terms are widely utilized by petroleum geologists. A petroleum system encompasses a hydrocarbon source rock and all generated oil and gas accumulations and includes all those elements that are essential for an oil and gas deposit to exist: petroleum source rock, migration path, reservoir rock, seal, and trap (Magoon, 1988a). The system has a stratigraphic limit, geographic extent, and time duration. Its name combines the names of the source rock and the reservoir rock and also expresses a level of certainty. Petroleum systems are classified by using criteria such as type of source and reservoir rock and the complexity of its geologic history, as explained in Magoon (1988b; table 1).

The list of petroleum systems within the United States (table 2) has been revised and expanded since the last tabulation in 1988, in which 119 systems were identified (Magoon, 1988b). As published information about U.S. petroleum systems becomes available, the list is revised to reflect this new information. Presently 130 petroleum systems have been identified, of which, 89 are purebred (structurally simple) and 41 are hybrid (structurally complex) (table 1). Of 12 possible categories, the 2 most common systems are in the purebred siliciclastic category and have either type II (32) or type III (19) source rocks (rocks containing type II or III organic matter). Presently, all hybrid carbonate systems contain type II source rocks. Siliciclastic reservoirs (90) occur more than twice as often as carbonate reservoirs (40). The most common source rock is type II (73), followed by type III (41), the least common being type I (16). For an explanation of kerogen types, see Tissot and Welte (1984).

Table 2 in this publication is reorganized from table 6 in Magoon (1988b). The petroleum systems in each category are arranged alphabetically. Rather than identifying their location by State, the geological provinces of the American Association of Petroleum Geologists are indicated for each system (Meyer, 1974; fig. 1, table 2), and the geological province code number along with the *Correlation of stratigraphic units in North America* (COSUNA) chart column number are shown. Because the petroleum system is independent of political boundaries (States), and may even be independent of sedimentary basins or arches, it is more appropriate to indicate the approximate geographic extent of each system using already established geological provinces.

Since the last tabulation in 1988, the list of petroleum systems within the United States has been expanded and revised to include 11 more systems and new information about previously identified systems (table 2). The 11 new systems are as follows: Chainman-Garrett Ranch(!)(Poole and Claypool, 1984), Desmoinesian-O sandstone(!)(Clayton, 1989), Mowry-Muddy(!)(Momper and Williams, 1984), Niobrara(!) (Rice, 1984), Niobrara/Carlisle-Frontier(!) (Momper and Williams, 1984), Ozette-Hoh(!)(Kvenvolden and others, 1988), Point Pleasant-Clinton(!)(Cole and others, 1987), Soda Lake-Painted Rock(.)(Lillis, 1988), Stillwater-Kulthieth(.)(Magoon, in press), Viola(!)(Jones and Philp, in press), and Woodford-Sycamore(!)(Jones and Philp, in press). Three petroleum systems have been reclassified from purebred to hybrid because the systems have been affected by either the Ouachita orogeny (Woodford/Chattanooga-Paleozoic(.)) or the Laramide orogeny (Aneth/Elbert-McCracken(?) and Tyler(!)). Five petroleum systems are reclassified from type III source to type II (G.E. Claypool, oral commun.; Cole and others, 1987); these are Devonian Black Shales-Venango(!), Ohio-Big Injun(.), Ohio Shale(!), Ohio-Weir(?), and Sumbury-Berea(!). The names of six petroleum systems have been changed: Bakken-Madison(.) is now Exshaw-Madison(.); Hue-Sagavanirktok/Canning(!) is now Hue-Sagavanirktok(!); Monterey-Sisquoc(.) is now Monterey-Tinaquic(.); Poul Creek-Katalla(?) is now Poul Creek(.); Salina-Niagaran(.) is now Salina A1-Niagaran(!); and Triassic-Newark(?) is now Newark(?). The level of certainty for four petroleum systems has been revised: Green River-Wasatch(.) is now Green River-Wasatch(!)(Tissot and others, 1978); Poul Creek-Katalla(?) is now Poul Creek(.)(Magoon, in press); Salina-Niagaran(.) is now Salina A1-Niagaran(!)(Gardner and Bray, 1984); and

[1]U.S. Geological Survey, Menlo Park, Calif.

Table 1. Distribution of the 130 identified U.S. petroleum systems according to categories of the petroleum system classification scheme

[Numbers in parentheses indicate number of petroleum systems of that category. An example petroleum system is recorded for each category in nomenclature column. Classification scheme is explained in Magoon (1988b)]

Geologic setting	Reservoir rock type	Source rock type	Nomenclature Source–reservoir (certainty)	Number of systems
Purebred (89)	Siliciclastic (58)	I	Green River–Wasatch(!)	7
		II	Heath–Tyler(!)	32
		III	Torok–Nanushuk(.)	19
	Carbonate (31)	I	Austin Chalk(!)	8
		II	Smackover(!)	16
		III	Chattanooga–Fort Payne(.)	7
Hybrid (41)	Siliciclastic (32)	I	Sheep Pass–Garrett Ranch(!)	1
		II	Ellesmerian(!)	16
		III	Tuxedni–Hemlock(.)	15
	Carbonate (9)	I	None	0
		II	Winnipeg–Red River(!)	9
		III	None	0
			Total	130

Table 2. Revised, reorganized, and expanded list of petroleum systems within the United States

[Level of certainty: (!), known; (.), hypothetical; (?), speculative; for certainty definitions see Magoon, 1988b]

AC, Atlantic Coast region (Jordan and Smith, 1983)
CCA, Central California region (Bishop and Davis, 1984a)
CSR, Central and Southern Rockies region (Kent and others, 1988)
GB, Great Basin region (Hinze, 1985)
GC, Gulf Coast region (Braunstein and others, 1988)
MBA, Midwestern Basin and Arches region (Shaver, 1985)
MC, Mid-Continent region (Adler, 1987)
NAL, Northern Alaska region (Schaff and Gilbert, 1987a)
NAP, Northern Appalachian region (Patchen and others, 1985a)
NCA, Northern California region (Bishop and Davis, 1984b)
NE, New England region (Skehan, 1985)
NMC, Northern Mid-Continent region (Bergstrom and Morey, 1985)
NRW, Northern Rockies/Williston basin region (Ballard and others, 1983)
NW, Northwest region (Hull and others, 1988)
PBR, Piedmont/Blue Ridge region (Higgins, 1987)
SAL, Southern Alaska region (Schaff and Gilbert, 1987b)
SAP, Southern Appalachian region (Patchen and others, 1985b)
SCA, Southern California region (Bishop and Davis, 1984c)
SSMC, Southwest/Southwest Mid-Continent region (Hills and Kottlowski, 1983)
TOT, Texas-Oklahoma Tectonic region (Mankin, 1987)
CSD/C, Geological province code number (Meyer, 1974)/COSUNA chart stratigraphic column number

Petroleum systems Source–reservoir(certainty)	Petroleum type	Geographic/stratigraphic location Region	CSD/C
PUREBRED, siliciclastic reservoir			
Type I source			
Austin Chalk/Eagleford–Woodbine(?)	Oil	GC	220;260/3,6,10
Cabot Head–Medina(.)	Oil	NAP	160/21
Glenwood–Rose Run(?)	Oil	NAP	160/8
Green River–Wasatch(!)[1]	Oil	CSR	575/17
Neogene–Salt Lake(?)	Oil	GB	625/15
Pennsylvanian cannel coals–sandstone(.)	Oil	NAP;SAP	160/1
Rose Hill–Keefer(?)	Gas	NAP	160/7-10
Type II source			
Conasauga–Rome(.)	Oil	NAP;SAP	160/20
Curtis–Entrada/Morrison(?)	Oil	CSR	535;595/13
Devonian–Berea(?)	Oil	MBA	305/3-6
Devonian Black Shales–Venango(!)[2]	Gas/oil	NAP	160/17,21
Eel River–Rio Dell(?)	Gas	NCA	720/1-2
Heath–Tyler(!)	Oil	NRW	510/12
Hue–Sagavanirktok(!)[3]	Oil	NAP	890/5-6
Kreyenhagen–Gatchell(?)	Oil	CCA	745/16-21,27-29
Lower Cretaceous–Paluxy(?)	Oil/gas	GC	210;220;230;260
Michigan–Stray(.)	Oil/gas	MBA	305/4-6
Miocene(?)	Oil	CCA	735/6
Monterey(?)	Oil	CCA	725/3
Monterey–Puente(!)	Oil	SCA	760/8-11

Table 2. Revised, reorganized, and expanded list of petroleum systems within the United States—Continued

Petroleum systems Source–reservoir(certainty)	Petroleum type	Geographic/stratigraphic location Region	 CSD/C
PUREBRED, siliciclastic reservoir			
	Type II source—Continued		
Monterey–Repetto/Pico(.)	Oil	SCA	755/4-5
Monterey–Tinaquaic(.)[3]	Oil	CCA;SCA	740;750/2
Monterey–Stevens/Kern River(.)	Oil	CCA	745/16-21,27-29
Moreno(?)	Oil	CCA	745/29
Mowry–Muddy(!)[4]	Oil	CSR	540/20
New Albany(.)	Gas	MBA	315/7-12,19-21
Newark(?)[3]	Oil	NE;PBR	100/8;150/11
Nonesuch–Keweenawan(?)	Gas	MC;NMC	310/20-21;320;325;370/10;380
Ohio–Big Injun(.)[2]	Gas/oil	NAC	160/8
Ohio Shale(!)[2]	Gas/oil	NAP;SAP	160/1
Ohio–Weir(?)[2]	Gas	NAP;SAP	160/1
Point Pleasant–Clinton(!)[4]	Oil	NAP	160/15-16
Soda Lake–Painted Rock(.)[4]	Oil	SCA	750/1
Sunbury–Berea(!)[2]	Oil/gas	MBA;NAP	300/16,18;160/1-3,7-8
Tuscaloosa(.)	Gas	GC	220/10
Unkown–Eocene(?)	Oil	GC	210;220;230;260/5,7,10,11
Unknown–Eutaw/Selma(?)	Oil	GC	210;260/6,12,13
Unknown–San Miguel/Olmos(?)	Oil	GC	220/1
Woodford–Silurian/Devonian(.)	Oil	SSMC	430/18-21
	Type III source		
Antrim(.)	Gas	MBA	305/15
Beluga–Sterling(.)	Gas	SAL	820/13
Cenozoic(.)	Oil/gas	GC	220/2-4,10-11
Chester(?)	Gas	TOT	200/17-19
Cotton Valley(?)	Gas	GC	210;230;260
Cretaceous(.)	Gas/oil	CSR	535/12-14
Cretaceous(!)	Gas	MC;NMC;NRW	320;380;390;395;515
Forbes(.)	Gas	NCA	730/23-24
Hombrook(?)	Gas	NCA	715/5
Jurassic–Cretaceous(?)	Gas	Atlantic offshore	-
Marcellus–Oriskany(.)	Gas	NAP	160/1-3,8-14
Miocene(.)	Gas	GC	210/14,16,17
Mississippian coals–sandstones(.)	Gas	SAP	160/25-26
Pennsylvanian coals(!)	Gas	NAP;SAP	160/1-2,7-9,12-13
Pennsylvania–Late Paleozoic(!)	Gas	MC;SSMC;TOT	335;345/4-5;350/6;355;360/27-29 365;370/26;375/25;440
Starkey–Winters(.)	Gas	NCA	730/26
Stepovak–Bear Lake(.)	Gas	SAP	845/10-11
Sunbury–Murrysville(.)	Gas	NAL	160/17-19
Torok–Nanushuk(.)	Oil	NAL	890/1-3
PUREBRED, carbonate reservoir			
	Type I source		
Athens–Trenton/Knox(?)	Oil	NAP;SAP	160
Austin Chalk(!)	Oil/gas	GC	220/1,4,5,11
Glenwood–Trempealeau(?)	Gas	NAP	160/15
Salina–Newburg(?)	Oil	NAP	160/16
Simpson–Viola(!)	Oil	MC;SSMC;TOT	335;350/6;355/1-2;360/27;365 370/26;375/25
Simpson–Viola/Hunton(.)	Oil	MC	335/21
Trenton(!)	Oil	MBA	300/13-14;315/7-12,19-21
Utica–Trenton(!)	Gas	MBA;NAP;NE	110;160/20;300

Table 2. Revised, reorganized, and expanded list of petroleum systems within the United States—Continued

Petroleum systems	Petroleum	Geographic/stratigraphic location	
Source–reservoir(certainty)	type	Region	CSD/C
PUREBRED, carbonate reservoir			
Type II source			
Conasauga–Knox(?)	Oil	SAP;TOT	160/1-8;200/17-19
Devonian–Detroit River/Traverse(?)	Oil	MBA	305/3-6
Desmoinesian–O sandstone(!)[4]	Oil	CSR	540/20
Dollar Bay(.)	Oil	GC	140/31
EauClair–Knox(?)	Gas	MBA	315/9-12,19-21
Niobrara(!)[4]	Gas	CSR	540/21;450/31
Niobrara/Carlisle–Frontier(!)[4]	Oil	CSR	540/20–21
Ordovician–Prairie du Chien/Black River/Trenton(?)	Oil	MBA	300/14-16;305/3-6,15
Pennsylvanian(.)	Oil	SSMC	430/18-19
Pennsylvanian(.)	Oil	SSMC	430/20-21
Permian(.)	Oil	SSMC	430/18-19
Permian(.)	Oil	SSMC	430/20-21
Salina A-1–Niagaran(!)[1,3]	Oil	MBA	305/3-6
Simpson–Ellenberger/Simpson(.)	Gas/oil	SSMC	430/19-21
Smackover(!)	Oil	GC	210;220;230;260
Sunniland(!)	Oil	GC	140/31
Type III source			
Chattanooga–Fort Payne(.)	Oil/gas	SAP	160/11-13
Marcellus–Bass Islands(.)	Gas	NAP	160/21
Marcellus–Onondaga(.)	Gas	NAP	160/22
Monroe(?)	Gas	GC	230/9
Ohio/Chattanooga–Comiferous(?)	Oil/gas	MBA;SAP	160/18;300/25
Ohio/Sunbury–Greenbriar/Newman(?)	Gas	NAP;SAP	160/1-2,18,21
Sligo(?)	Gas	GC	220/5,7,14
HYBRID, siliciclastic reservoir			
Type I source			
Sheep Pass–Garrett Ranch(!)[1]	Oil	GB	625/9,11
Type II source			
Aneth/Elbert–McCracken(?)[5]	Oil	CSR	585/23
Aspen/Bear River–Nugget/Madison(?)	Oil	CSR	535;570/11
Chainman–Garrett Ranch(!)[4]	Oil	GB	625/11
Chainman–White Rim(?)	Oil	CSR;GB	585;630/29
Domengine–Cierbo/Briones(?)	Oil/gas	CCA	725/1
Ellesmerian(!)	Oil	NAL	890/1-6
Greenhorn–Dakota(.)	Oil	CSR	580/29
Jurassic/Cretaceous(?)	Oil	NRW	500/10,11;505/6,7;510/12
Mancos–Mesaverde(.)	Gas	CSR	580/29
Mancos–Tocito(.)	Oil	CSR	580/29
Minnelusa(!)	Oil	CSR	515;540/6
Phosphoria–Weber(!)	Oil	CSR	505-535;570;575;615;630
Todilto–Entrada(.)	Oil	CSR	580/29
Tyler(!)[5]	Oil	NRW	395/19
Utica–Beekmantown(!)	Gas	NE	100/14
Woodford/Chattanooga–Paleozoic(.)[5]	Oil	MC;SSMC;TOT	335;345/4-5;350/6;355;360/27-29 365;370/26;375/25;385;440;450
Type III source			
Cretaceous(?)	Oil/gas	CSR	520/4
Cretaceous(?)	Oil	CSR	530/8
Cretaceous(?)	Oil/gas	CSR	540/21
Cretaceous(?)	Oil	CSR	515/6
Cretaceous(?)	Gas	CSR	535/9,15

Table 2. Revised, reorganized, and expanded list of petroleum systems within the United States—Continued

Petroleum systems	Petroleum	Geographic/stratigraphic location	
Source–reservoir(certainty)	type	Region	CSD/C
HYBRID, siliciclastic reservoir			
	Type III source—Continued		
Cretaceous(?)	Gas	CSR	545/20
Cretaceous–Tertiary(?)	Gas	CSR	500/4
Cretaceous–Tertiary(!)	Gas	CSR	530/8
Lewis–Picture Cliffs(.)	Gas	CSR	580/29
Mesaverde(.)	Gas	CSR	575/17
Mesaverde(.)	Gas	CSR	595/18
Ozette–Hoh(!)[4]	Oil	NW	710/14
Poul Creek(.)[1,3]	Oil	SAL	810/24
Stillwater–Kulthieth(.)[4]	Oil	SAL	810/24,26-27
Tuxedni–Hemlock(.)	Oil	SAL	820/13
HYBRID, carbonate reservoir			
	Type II source		
Bakken–Madison(!)	Oil	NRW	395/13-20
Chainman–Simonson(?)	Oil	GB	625/11,12,17,18,20
Conasauga–Knox(?)	Gas	PBR	150/4-6
Exshaw–Madison(.)[3]	Oil	NRW	500/7,10,11;505
Favret(?)	Oil	GB	625/2
Paradox–Hermosa(.)	Oil	CSR	585/23
Winnipeg–Red River(!)	Oil	NRW	395/13-20
Woodford–Sycamore(!)[4]	Oil	TOT	350/6
Viola(!)[4]	Oil	TOT	350/6

[1]Level of certainty revised.
[2]Reclassified petroleum system from type III source.
[3]Petroleum system name revised.
[4]Newly identified petroleum system.
[5]Reclassified petroleum system from purebred.

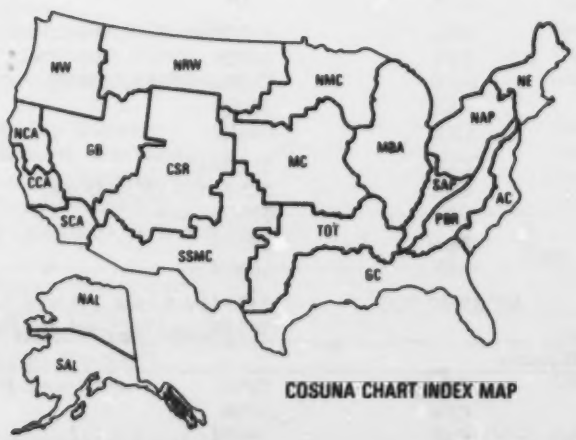

Figure 1. Index map of regions for the *Correlation of stratigraphic units of North America* (COSUNA) charts. See table 2 for region names and references.

Sheep Pass-Garrett Ranch(.) is now Sheep Pass-Garrett Ranch(!)(Poole and Claypool, 1984). These additions and revisions are footnoted on table 2.

Many of the petroleum systems of the "known" level of certainty are documented in the literature. In a known petroleum system, in the case of oil, a good geochemical match must exist between the source rock and the oil accumulations; or, in the case of natural gas, the gas is produced from a gas source rock. Of the 35 known systems, 25 are documented in the literature (table 3).

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Table 3. References where oil/source rock correlation demonstrate a known petroleum system

Petroleum system Source–reservoir(certainty)	Reference
Austin Chalk(!)	Hunt and McNichol, 1984
Bakken–Madison(!)	Dow, 1974; Williams, 1974
Chainman–Garrett Ranch(!)	Poole and Claypool, 1984
Cretaceous(!)	No reference
Cretaceous–Tertiary(!)	No reference
Desmoinesian–O sandstone(!)	Clayton, 1989
Devonian Black Shales–Venango(!)	No reference
Ellesmerian(!)	Seifert and others, 1980; Sedivy and others, 1987
Green River–Wasatch(!)	Tissot and others, 1978
Heath–Tyler(!)	Rinaldi, 1988
Hue–Sagavanirktok(!)	Anders and others, 1987 Anders and Magoon, 1985
Minnelusa(!)	Clayton and Ryder, 1984
Monterey–Puente(!)	No reference
Mowry–Muddy(!)	Momper and Williams, 1984
Niobrara(!)	Rice, 1984
Niobrara/Carlile–Frontier(!)	Momper and Williams, 1984
Ohio Shale(!)	No reference
Ozette–Hoh(!)	Kvenvolden and others, 1988
Pennsylvanian coals(!)	No reference
Pennsylvania–Late Paleozoic(!)	No reference
Phosphoria–Weber(!)	Momper and Williams, 1984
Point Pleasant–Clinton(!)	Cole and others, 1987
Salina A-1–Niagaran(!)	Gardner and Bray, 1984
Sheep Pass–Garrett Ranch(!)	Poole and Claypool, 1984
Simpson–Viola(!)	No reference
Smackover(!)	Claypool and Mancini, 1989; Oehler, 1984; Sassen, 1989
Sunbury–Berea(!)	Cole and others, 1987
Sunniland(!)	Palacas and others, 1984
Trenton(!)	Reed and others, 1986
Tyler(!)	Dow, 1974; Williams, 1974
Utica–Beekmantown(!)	No reference
Utica–Trenton(!)	No reference
Viola(!)	Jones and Philp, submitted
Winnipeg–Red River(!)	Dow, 1974; Williams, 1974
Woodford–Sycamore(!)	Jones and Philp, submitted

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The Value of Stratigraphic Cross Sections

By Cornelius M. Molenaar[1]

INTRODUCTION

In recent years, the great proliferation of geologic literature has made it ever more time consuming for geologists to keep up with the latest concepts and developments, even in only one geologic specialty. Many geologists may only read an abstract of a report and briefly review the figures. For this reason, it is important that authors carefully prepare their illustrations to show as clearly as possible the concepts or details they are trying to convey. The old adage that "one picture is worth a thousand words" could never be truer, especially when many readers never thoroughly read a paper. This report is a brief discussion on the value of one type of illustration, the stratigraphic cross section, which is an excellent method of graphically showing vertical and lateral lithostratigraphic relations.

Some cross sections are schematic (cartoons) and are intended to show only overall relations without regard to scale, precise location, and actual details. Others are constructed using "hard" data, such as data from boreholes or measured sections. This latter type takes more time and effort to construct, but shows the basic data to support the interpretations. The following discussion relates to these data-based stratigraphic sections.

DATA, AND SIZE AND SCALE OF ILLUSTRATION

Data used in constructing stratigraphic cross sections are usually derived from measured outcrop sections or geophysical logs of boreholes. The combination of data from outcrop sections and borehole logs adds immeasurably to detailed stratigraphic studies. If the quality of outcrops is good, surface sections are much better than borehole logs for interpreting details of lithology, contact relations, bedding features, and depositional environments. Conversely, borehole logs are generally much better for measuring thicknesses, correlating marker beds in shale sections, and showing lateral relations of subjacent lithologic units. Thus the two types of data complement each other.

Depending on the scale and size of the illustration (that is, page size or large plate size) measured outcrop sections or borehole logs can be used to show the graphic data, or vertical lines ("stick" sections) can be substituted for the data when space or size is limited. Whichever type is used, it is important to plan the layout carefully to make maximum use of the available space. If more than one cross section is planned to show relations across different parts of the basin or area of interest, the same vertical scale should be used, if feasible, to aid direct comparisons of the different sections. When constructing a line of section through numerous control points, such as borehole logs or outcrop sections, positioning the control points relative to their actual horizontal separation is helpful in order to best show rates of change of lithologic units or rates of convergence or divergence. This positioning is a simple matter if vertical stick sections are used for each control point. But if the actual borehole logs or graphic columnar outcrop sections are used, allow for the addition of an average width of the borehole logs or columnar sections in addition to the distance between control points.

The choice of vertical and horizontal scales depends on the size of the illustration and the purpose of the cross section. If a regional overview is the objective, a section must be prepared at a small scale, but details will be somewhat generalized. Larger scales should be used to show stratigraphic details of a specific lithologic unit. A cross section in Molenaar and others (1986) is an example of a small-scale stratigraphic cross section. This section shows a 355-mi (570 km)-long subsurface section across the North Slope of Alaska using gamma-ray and resistivity logs of 18 boreholes at a vertical scale of 1:24,000 and horizontal scale of approximately 1:870,000 (1 in.= 14 mi or 1 cm= 8.7 km). Vertical exaggeration is about 36X. Even at this scale, the log character substantiates most of the correlations shown. Plate-size cross sections in Hook and others (1983) are examples of moderate-scale cross sections. Two sections show correlations of numerous measured outcrop sections of approximately 1,000 ft (300 m) of middle Cretaceous rocks in west-central New Mexico. The vertical scale is about 1:1,900 (the unusual scales are due to photographic reduction of the work sections) and the vertical exaggerations are about 146 and 256X. At this scale, the lithologic details that are shown support the correlations of rock units. In addition, numerous molluscan fossils are listed where they occur on the sections. The detailed

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sections in Hook and others (1983) are also shown as less detailed page-size figures in which vertical lines (sticks) are substituted for the actual measured section. Supplemental page-size figures permit the reader to visualize the overall relations; the larger plates can be unfolded if the reader wants to inspect the details.

DATUMS

Choosing a datum is also an important consideration in constructing cross sections. Again, it depends on the features the author wants to show. To illustrate the stratigraphic details of a particular formation, it is best to use a horizontal datum a short distance above the formation. In some cases, using a datum below the formation of interest, even though correctly correlated, can make lateral relations appear quite different, especially if the section thickens or a stratigraphic rise occurs between control points. On some cross sections a variable datum is appropriate, such as a section where the control in one part of the section does not include higher (or lower) parts of the stratigraphic interval included in other parts of the cross section. On cross sections showing numerous correlated marker beds, a specific datum is not actually necessary.

Using sea level or an elevation above or below sea level as a datum will show formations at their present structural positions. Showing structure between control points is inadvisable unless it is desirable to show the projected formations at their low point in a basin or their high point on a structural high. But trying to show details of folding and faulting (unless they are syndepositional) and still show details of stratigraphy is difficult because the vertical scale necessary for detailed stratigraphic sections is vastly different from an appropriate scale for structure cross sections.

Commonly, an unconformity or the base of a marine transgression is used as a datum. Both of these surfaces are usually essentially flat surfaces prior to deposition of overlying strata. Their use as a datum illustrates the post-truncation relations of underlying strata. In some cases, however, unconformities can have significant relief. Such surfaces should be avoided for use as flat datums.

USE OF TIME MARKER BEDS

In constructing a stratigraphic cross section, the correlation of many marker beds (time lines) both above and below the rock unit of interest provides a time-bounded framework that greatly aids in illustrating and understanding the depositional architecture. Usually there are many correlatable marker beds in marine shale sequences, such as the Upper Cretaceous Mancos Shale or equivalents in the Western Interior seaway, that can be recognized on geophysical logs of boreholes, especially on the conductivity log. Recognition of marker beds is facilitated by lithologic changes within marine shales. Some of these changes can be quite subtle. Bentonite beds and sandstone-shale contacts are examples of obvious changes. The subtle changes, which also are very reliable for long-distance correlations, are due to changes in content of carbonate, intermixed bentonite, and silt or sand within the shale section and possibly differences in clay mineralogy. All such lithologic variations are expressed by variations on resistivity or conductivity logs. Some markers are recognized as solitary deflections or spikes on the log. Others are recognizable resistivity or conductivity patterns over an interval of as much as 100 ft (30 m).

CONCLUSION

Detailed stratigraphic cross sections, using correlated time marker beds as well as lithologic units and a carefully selected datum (or datums), show not only the correlations of lithologic units, but how they correlate with respect to time lines. The large vertical exaggeration used in constructing most stratigraphic cross sections permits recognition and measurement of subtle depositional and paleostructural features, such as (1) diachronism and stratigraphic rising (relative sea-level rise) of shoreface sandstone bodies, (2) shelf to slope to basinal topography, if developed, in thick marine shale sequences, (3) low-amplitude paleostructural features, and (4) differential compaction features associated with lateral heterogeneities in sand-shale sections. The plates in Molenaar and Baird (1989) show examples of subsurface correlations across the northern part of the San Juan basin in southwest Colorado using time marker beds to illustrate some of the above-listed features.

In summary, properly constructed stratigraphic cross sections are an excellent method for depicting obvious and subtle stratigraphic features. Unlike maps that show isopachs of specific intervals (either time bounded or facies bounded), isoliths, or generalized lithofacies distribution patterns, stratigraphic sections show how the rocks fit together, and meaningful stratigraphic sequences in the order that they were deposited. Moreover, by annotation, much additional data can be shown on the cross sections, such as geochemical, paleontologic, petrologic, and hydrocarbon test or completion data.

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Carbonate Aprons—Their Petroleum Reservoir Potential

By Harry E. Cook[1] *and* Henry T. Mullins[2]

INTRODUCTION

Occurrence of Allochthonous Carbonate Debris

Sediment gravity-flow deposition along the deep-water flanks of carbonate platforms typically does not produce submarine fans. Instead, wedge-shaped *carbonate aprons* develop parallel to the adjacent shelf-slope break (Schlager and Chermak, 1979; Crevello and Schlager, 1980; Cook, 1983a; Mullins, 1983, 1986; Mullins and Cook, 1986; Sarg, 1988). The major difference between submarine fans and carbonate aprons is a point source with channelized sedimentation on fans, versus a line source with sheet-flow sedimentation on aprons.

Modern and ancient siliciclastic deposits formed by sediment gravity flows have been reported from a wide variety of geologic settings throughout the geologic record (for example, Nelson and others, 1970; Cook and others, 1982; Howell and Normark, 1982; Walker, 1984; Bouma and others, 1985; Shanmugam and Moiola, 1988). Likewise, since the late 1960's it has been known that carbonate mass-transport deposits occur virtually throughout the Phanerozoic in widely diverse tectonic and stratigraphic settings (for example, Thomson and Thomasson, 1969; Cook and others, 1972; Mountjoy and others, 1972; Wilson, 1975; Cook and Enos, 1977; Cook, 1979; Mullins and Neumann, 1979; Cook and others, 1983; Cook and Mullins, 1983; Crevello and Harris, 1985; Bourrouilh and Doyle, 1987; Cook and others, 1989a). It is normal to find allochthonous carbonate sediments in carbonate slope, base-of-slope, and basin-plain sequences (Cook and Mullins, 1983), regardless of the type of carbonate platform (Read, 1982) or the type of carbonate slope margin (Mullins, 1978; Cook, 1983a; James and Mountjoy, 1983; McIlreath and James, 1984).

INTERPRETATION AND SIGNIFICANCE

Early studies tended to interpret carbonate petroleum reservoirs consisting of coarse-grained carbonate sandstones and conglomerates as representing shoal-water carbonate facies (for example, Barnetche and Illing, 1956). Later studies, however, showed that some of these facies had been misinterpreted and that the reservoirs actually consisted of allochthonous carbonate sediments, the constituents of which had been transported tens of kilometers from bank and reef margins by turbidity currents and debris flows (for example, Viniegra and Castillo-Tejero, 1970; Cook and others, 1972; Cook, 1983b; Enos, 1977). Even so, industry did not begin to actively explore for deep-water carbonate turbidite or debris-flow reservoirs until the early 1980's. Furthermore, outcrop studies of allochthonous carbonate debris did not focus on their reservoir potential but rather on their uses: (1) for signaling the existence of carbonate buildups or reefs in an area, (2) as proximity indicators for locating potential petroleum reservoirs in shoal-water carbonate environments, (3) for correlation in the basin facies, and (4) for genetic interpretation of the morphologic development and diagenesis of carbonate complexes (Cook and others, 1972; Mountjoy and others, 1972).

CARBONATE APRON MODELS

Background

The submarine fan model (Nelson and others, 1970; Mutti and Ricci Lucchi, 1978; Normark, 1978; Walker, 1978), as well as its variations (Bouma and others, 1985; Shanmugam and Moiola, 1988), is well established in the geologic literature and is widely used both for paleoenvironmental interpretations of coarse-grained, deep-sea facies and as a predictive tool in the exploration for petroleum from deep-water reservoirs. Although the model has had considerable success in application to siliciclastic facies, studies of both modern carbonate mass-transport sequences (Mullins, 1978, 1983, 1986; Mullins and Neumann, 1979; Schlager and Chermak, 1979; Crevello and Schlager, 1980; Mullins and others, 1984) and ancient ones (Koss, 1977; Biddle, 1979; Kepper, 1981; Jordan, 1981; Cook, 1982, 1983a) have clearly demonstrated that the submarine-fan model cannot be applied unequivocally to carbonate-sediment gravity-flow deposits. Instead of orderly stratigraphic sequences of outer, middle, and inner fan facies that originate from a point source, many ancient carbonate mass-transport deposits consist of a seemingly random

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distribution of debris that has more affinity with the debris-sheet model (Cook and others, 1972) and apron model (Cook, 1983a; Mullins and Cook, 1986). In fact, documented examples of ancient carbonate submarine fans with recognizable fan facies are quite rare (for example, Cook and Egbert, 1981; Cook, 1983b; Ruiz-Ortiz, 1983; Wright and Wilson, 1984; Watts, 1985, 1986; Cook and others, 1989a,b), and to date no complete modern examples have been discovered (Mullins and Cook, 1986). Despite this, numerous papers in the literature have indiscriminately used the term "fan" or "submarine fan" in their discussion of carbonate mass-flow facies sequences without presenting evidence that documents the existence of distinct fan facies associations. Unlike aprons, submarine fans develop at the mouth of large submarine canyons by mass-flow processes that are typically well channelized. Thus, one basic criterion that distinguishes fans from aprons is the high percentage of channelized facies in fans versus the dominance of non-channelized sheet-flow facies in aprons (Mullins and Cook, 1986).

In the rock record, two distinct types of carbonate aprons have been recognized (Cook, 1983a; Mullins and Cook, 1986) the *slope apron* and *base-of-slope apron* (fig. 2). The major difference between the two models is that the base-of-slope model involves an upper-slope bypass zone, whereas in the slope apron model, redeposited carbonates extend up to the shelf edge without an intervening bypass slope.

Slope Apron

Slope aprons are most abundant along carbonate platform margins that have a relatively gentle gradient (less than 4 degrees) into the adjacent basin, such as the Upper Devonian Ancient Wall and Miette carbonate banks in Alberta, Canada, as well as the Upper Silurian to Lower Devonian of central Nevada (Cook, 1983a; Cook and Taylor, 1987). In the slope-apron model, carbonate gravity flow deposits extend up to the adjacent shelf-slope break without an upper slope bypass zone. Turbidity current and debris-flow deposits are abundant in slope aprons, but they do not develop systematic vertical cycles (fig. 2). Carbonate slope aprons have yet to be identified in modern environments, even those platform margins with slopes of less than 4 degrees (Mullins and Cook, 1986). The reason for this is not clear although it may be due to the fact that modern platforms tend to have relatively high relief. Future studies of upper slopes in modern environments may reveal the presence of slope aprons.

Base-of-Slope Carbonate Apron

Base-of-slope apron sediments (fig. 2) bypass upper slopes via numerous small gullies and canyons, as well as by sheet-flow events. This kind of carbonate apron develops along relatively steep (greater than 4 degrees) high-relief platform margins, such as those in parts of the Upper Devonian and Lower Mississippian of the Great Basin or the Permian of west Texas (Cook, 1983a, b; Cook and Taylor, 1987), and the Carboniferous of east-central Alaska (Cook and others, 1987). These examples exhibit thickening-upward cycles (fig. 2). The relatively steep bypass slopes commonly have numerous submarine slides and slumps; this is in contrast to carbonate slope aprons, which are rarely associated with submarine slides and slumps.

In the northern Bahamas, well-developed modern base-of-slope carbonate aprons have been described from the Little Bahama Bank (Mullins, 1985; Mullins and others, 1984), southern Tongue of the Ocean (Schlager and Chermak, 1979), and Exuma Sound (Crevello and Schlager, 1980; Austin and others, 1986, 1988).

PETROLEUM EXPLORATION FOR CARBONATE APRONS

Deep-water, carbonate sediment-gravity-flow deposits are now recognized as very important and attractive reservoirs for petroleum (Cook and Enos, 1977; Scholle, 1977; Mullins and Cook, 1986). A good example of extensive petroleum production from an ancient base-of-slope carbonate apron is the Cretaceous Tamabra Limestone of Mexico, where production and proven reserves exceed 2.3 billion barrels of oil (Enos, 1977, 1985; Enos and Moore, 1983). Production is mainly from solution porosity in grainstone-packstone sediment gravity flow facies that are encased in fine-grained, deep-water deposits (Enos, 1977, 1985).

Numerous giant oil fields also have been recently discovered in the "Great Carbonate Bank of Yucatan" of southern Mexico and offshore Campeche, which has been considered to be a major world petroleum province (Meyerhoff, 1980; Viniegra, 1981). One of the largest fields is a stratigraphic trap, where detrital calcarenites wedge out into finer grained facies (Viniegra, 1981), in a fashion possibly similar to the idealized base-of-slope carbonate apron. As of 1979, proven reserves for this petroleum province exceeded 18 billion barrels of oil and 15 trillion cubic feet of gas (Meyerhoff, 1980; Viniegra, 1981).

More recent petroleum discoveries in the southeast area of Mexico's Reforma-Jalpa were reported by Aguayo and others (1985). There, Upper Jurassic and Lower Cretaceous carbonate petroleum reservoirs occur in platform and slope environments. The basin and carbonate platform are separated by a slope 20 km wide. Carbonate slope sediments are described as being formed of "breccia beds interlayered and interfingered with pelagic horizons" (Aguayo and others, 1985). Pro-

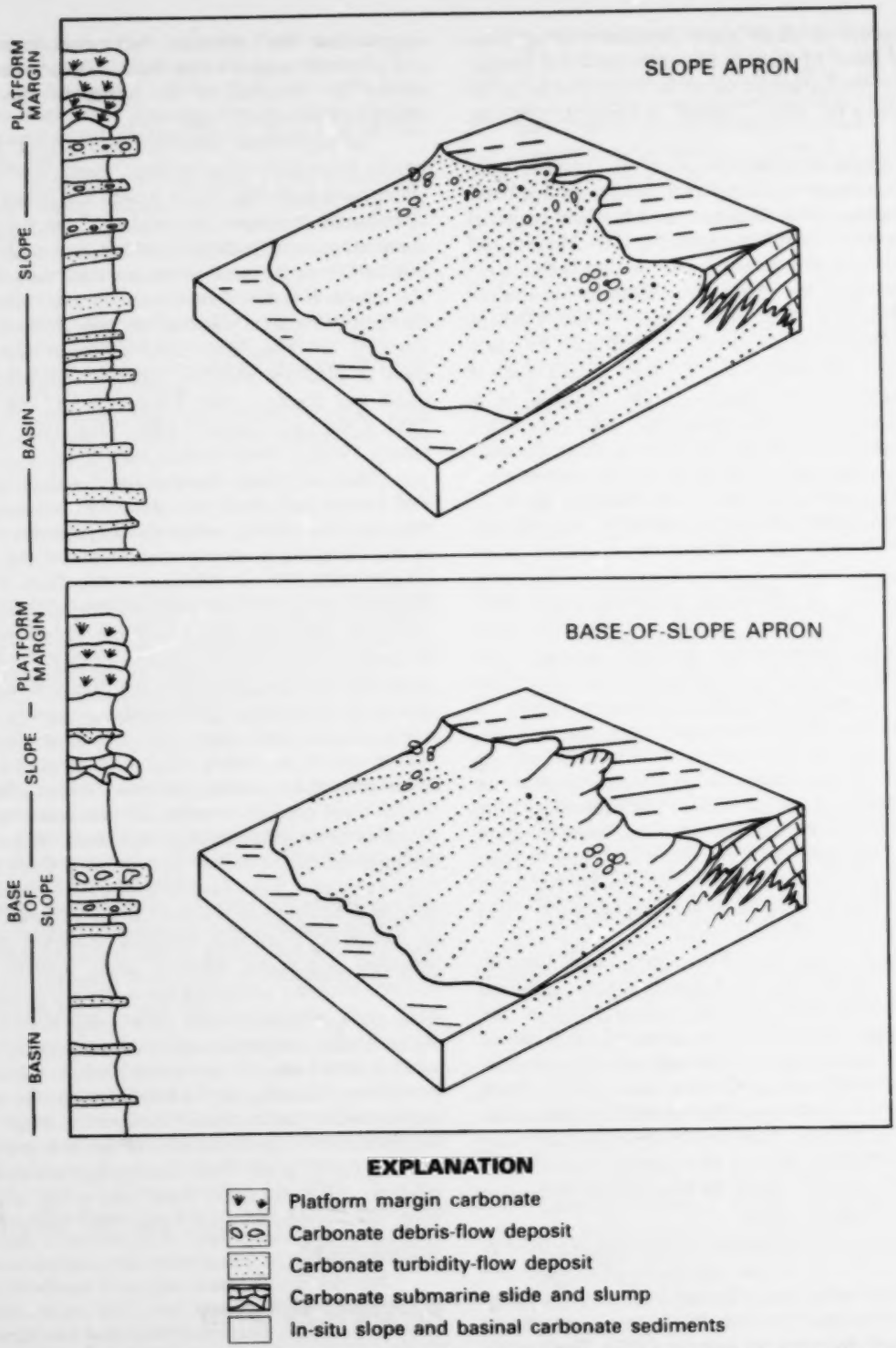

Figure 2. Schematic, three-dimensional block-diagram models for carbonate slope apron and base-of-slope apron. Along left-hand margins are highly generalized seaward-prograding stratigraphic sequences that one might expect to find associated with these apron models. From Cook (1983a) and Mullins and Cook (1986).

duction occurs in these slope breccias starting from about 5 to about 12 km seaward of the platform margin. As of 1985, production occurred for a distance of 15 km laterally along the slope (Aguayo and others, 1985, fig. 7).

Petroleum reserves also occur in Permian deep-water carbonate gravity-flow facies along slope and base-of-slope settings in the Delaware and Midland basins of west Texas (Cook, 1983a,b; Mazzullo, 1984; Hobson and others, 1985a,b). We do not know whether these reservoirs represent debris sheets, fans, carbonate aprons, or some combination of all three models (Cook, 1983a,b; Mazzullo, 1984; Hobson and others, 1985a,b). Probably allochthonous carbonate deposits extend around much of the Permian platform margin in the Midland basin (Mazzullo, oral communication, 1983; Mazzullo, 1984; Mazzullo and Reid, 1987). Oil fields in these Permian carbonate rocks occur 15 to 30 km seaward from platform margins, extend basinward for distances up to 25 km, and are about 40 km long parallel to the slope (Cook, 1983b). Production occurs from megabreccias, grain-supported conglomerates, and pebbly calcarenites. Much of the porosity is secondary, resulting from post-depositional dissolution of unstable aragonite and magnesian calcite constituents. Fracture porosity and intercrystalline dolomitic porosity are also important. Downslope transport probably involved a variety of mechanisms including submarine slides, debris flows, and turbidity-current flows. Many of the boulder-bearing megabreccia debris flows may have originated as platform-margin-generated slides. The transition from sliding to debris flow to turbidity-current flow is a subject studied by Hampton (1972) in laboratory experiments and for subaerial mass-transport deposits, by Field and Clarke (1979) on modern siliciclastic slopes, and by Cook (1979) on ancient carbonate slopes.

In the Pennsylvanian Palo Duro basin, Crevello and others (1985) described allochthonous sediment gravity-flow carbonate rocks that occur in slope and basinal settings. One well produced nearly 4,000 barrels of oil before abandonment. Although not a commercial success, the discovery, as Crevello and others (1985) pointed out, is important as it documents the first occurrence of oil production from slope and basinal carbonate debris in the Palo Duro basin. The nearest oil production is 80 km to the south in platform-margin carbonate rocks (Crevello and others, 1985).

New potential exploration targets exist in a frontier area of east-central Alaska where a 500-m-thick sequence of Carboniferous carbonate base-of-slope apron and (or) submarine fan-lobe facies are spectacularly exposed (Cook, Magoon, and others, 1987). The organic content of the lime mudstones interbedded with the allochthonous carbonate rocks averages 5 weight percent, TAI, and T_{max} indicates that the organic matter is well into oil generation but not overmature. S_2/S_3 ratios suggest that the carbonate rocks contain mixed gas-and-oil-prone source rocks. Such source rock data document the potential of the apron or fan facies as subsurface petroleum reservoirs.

As exploration continues into deeper water carbonate slope and basinal settings, more reservoirs of the above types probably will be sought and found. It will be increasingly important to understand the nature, facies associations, and geologic controls responsible for the origin of these potential carbonate reservoirs. For example, a topic of active research involves the interrelations between carbonate platform margin collapse, eustatic sea-level lowering, and rapid sediment accumulation rates at platform margins (Mullins and others, 1986; Cook and Taylor, 1987; Cook, Taylor, and Magoon, 1987; Field and Gardner, 1987; Sarg, 1988; Cook and others, 1989a,b; Mullins and Hine, 1989).

Many of these coarse-grained, redeposited facies also have a high diagenetic potential that can enhance their reservoir quality within the deep marine diagenetic realm, particularly during shallow burial (Mullins and others, 1985; Dit and Mullins, 1988). Thus it becomes important to understand under what conditions unstable carbonate minerals may constitute these redeposited sequences. There are two principal types of redeposited carbonate particles: those that are platform derived and contain an abundance of metastable aragonite and magnesian calcite, and those that are slope derived and consist mainly of stable calcite. In terms of porosity enhancement by postdepositional solution, the former would have greater promise as petroleum reservoirs. Thus, an exploration strategy that seeks mineralogically unstable carbonate gravity-flow facies is likely to have a higher rate of success. Such an exploration strategy might use the following perspectives: along windward margins of carbonate platforms, on-bank transport of coarse sediment dominates, whereas along leeward margins coarse carbonate sediments are actively transported off-bank onto adjacent slopes (Hine and Mullins, 1983). Accordingly, carbonate-sediment gravity-flow facies along leeward margins are more likely to have a higher percentage of redeposited unstable aragonite and magnesian calcite and are more likely to undergo porosity enhancement by the dissolution of unstable grains (Mullins and Cook, 1986). This concept appears to be applicable to the Cretaceous Poza Rica trend, which Paul Enos (oral communication, 1985) has interpreted as a leeward margin.

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Deep-Water Fan Systems

By William R. Normark[1]

About the same time that Shepard and his peers had documented the widespread occurrence and types of submarine canyons and their importance in providing pathways for terrigenous sediment to reach the deep-sea floor (see review by Shepard and Dill, 1966), mapping of onshore turbidite deposits had begun to define the nature of the coarse-grained, fan-shaped deposits fed by ancient submarine canyons (Sullwold, 1960; Jacka and others, 1968). General depositional models for submarine fans began to appear shortly thereafter (Normark, 1970; Mutti and Ricci Lucchi, 1972), and the number of models and model variations has blossomed, especially during the last decade.

The three general types of studies used for the more common fan models are: (1) field (outcrop) mapping, (2) acoustic imaging of modern fans, and (3) seismic-stratigraphic studies. Models for "ancient" turbidite deposits are generally based on field work that in some cases can be augmented by analysis of borehole cores. The most widely used are facies models, which are primarily based upon interpretation of fan depositional environments through detailed vertical-section measurements from outcrop studies (Mutti and Ricci Lucchi, 1972, 1975; Ricci Lucchi, 1975; Mutti, 1977, 1979). "Morphologic," or modern-fan, models are based on the knowledge of the surface-shape characteristics of the fan system together with some general idea of the nature (grain size, composition, internal structure, and stratigraphic control) of the upper few meters or tens of meters of the fan sediments (Normark, 1970, 1978; Nelson, 1976). The study of modern fans with side-looking-sonar images and high-resolution seismic-reflection profiles (1–10 kHz) in conjunction with core data commonly provides an acoustic-facies scheme or facies combining acoustic characters and surficial-sediment type. Seismic-stratigraphic models are based on deep-penetration, but low-resolution, seismic-reflection profiles (Vail and others, 1977; Vail, 1987). This technique generally results in mapping only the large-scale features of deep-water fan systems, such as lobes or major channel-levee systems, but has the advantage of being suitable for either modern or buried systems whether in deep water or within filled basins along continental margins.

As more data became available for the relatively poorly documented modern submarine fans, some sedimentation models reflected an attempt to combine characters observed from work on modern and ancient deposits (for example, Nelson and Nilsen, 1974; Walker, 1978; see also review by Howell and Normark, 1982). Such attempts have not always met with general approval; see, for example, the discussion and reply sequence of the Walker paper (Nilsen, 1980; Normark, 1980; Walker, 1980). With the recognition of the strong imprint that sea-level changes have on the development of deep water clastic deposits, later models combine (or blend without specific attribution) observations from all three basic types of study (Vail and others, 1977; Mutti, 1985; Pickering and others, 1986; Vail, 1987; Shanmugam and Moiola, 1988). Many additional sedimentation-model variations of the basic themes described in the references above have resulted from modification of one or only a few components of an established general model to "better fit" a limited set of field observations, commonly from a poorly understood deposit. Such ad hoc models have limited use for interpretation of other turbidite systems.

All three model types and some of the various hybrid versions have been widely used but generally without recognizing (or admitting) the basic differences in the types of observations used. During the last half decade, however, an ever more common theme among fans (friends) of submarine fans has been to express concern over the general applicability and usefulness of existing models for submarine fan deposits, whether such models are concerned with deciphering depositional processes or predicting reservoir potential for hydrocarbon exploration (Mutti, 1984; Bouma and others, 1985; Normark and others, 1985; Shanmugam and Moiola, 1985; Shanmugam and others, 1985; Normark, 1986; Mutti and Normark, 1987). The questions raised in the references above were discussed in several international forums; reviews of most of the submarine fans and turbidite systems that have been studied to date are provided in two books covering these forums (Bouma and others, 1985; Weimer and Link, in press).

The first COMFAN (COMmittee on FANs) meeting in 1982 provided a chance to compare data from 23 modern and ancient turbidite systems. Participants at this workshop could not agree on common definitions for many of the terms used to describe fan features but did agree to a common set of criteria to present their

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research. The volume resulting from this meeting reviews 28 different turbidite systems and includes preliminary results from Leg 96 of the Deep Sea Drilling Program on the Mississippi Fan (Bouma and others, 1985). Although seismic-stratigraphic analyses were available for several turbidite systems discussed at COMFAN I, a special session at the 1987 Society of Economic Paleontologists and Mineralogists Midyear Meeting focused directly on the seismic stratigraphy of submarine fans. The results of this forum are presented in a book covering more than 15 turbidite systems (Weimer and Link, in press). The groundwork laid by these two meetings provided the background for the COMFAN II workshop in 1988, where all three approaches to the study of deep-water fans were incorporated (Mutti and others, in press). The examples that follow illustrate the types of interpretational discrepancies (discussed at the COMFAN meetings) that arise from utilizing different techniques to study submarine fans.

Fan divisions (implied depositional environments) based on examination of modern systems rely on morphologic characters such as the nature of the channels, average slope, and geographic position, but similarly named divisions for ancient turbidite deposits that are based on outcrop mapping or borehole studies are keyed to the nature of the sedimentary rock characters as determined from detailed vertical-section measurements, including bed thickness, grain size, and sedimentary structures, as well as the vertical (and in a few cases, horizontal) sequence(s) that may be exhibited using these characters. Interpretations of modern fans generally consider the basin-plain environment to be the most distal facies of and time-equivalent with the main fan body. On the other hand, at the coarser scale of observation obtained with seismic-stratigraphic data, major fan bodies are interpreted to prograde over basin-plain deposits of an earlier phase of basin development.

The use of the term lobe or depositional lobe shows the greatest variation between students of submarine turbidite systems (Mutti and Normark, 1987). The most widely referenced application of the term is based on the original work of Mutti and Ricci Lucchi (1972), whose classic examples are from turbidite systems formed in elongate basins within compressional margin settings. Their lobe features are tabular, channel-free, coarsening- and thickening-upward sandstone bodies that can extend for tens of kilometers parallel to the basin axis; these general characters are supplemented by facies distinctions based on the details of bedding features. Lobe distinctions based on seismic-reflection profiles, on the other hand, suggest that they are mounded features with downlap relations of internal reflectors at their margins (Mutti and others, in press). The definition of lobe features on modern fans follows neither of the sets of characters noted above (see the summary in Mutti and Normark, 1987); instead, the term "lobe" is applied variously to any area of sand deposition, with or without channels. The thickness of the lobes from modern fans is generally not determined (being too thin to be resolved with the low-frequency reflection profiles needed to achieve subbottom penetration in sandy environments), and the nature of the sediment composing the lobes is based on short surficial core samples from the upper few meters of the deposit.

Our understanding of modern fans is strongly tied to our interpretation of the shape of the deposit, even though for most fans we do not have precise morphologic control. Long-range side-looking sonar images have shown a remarkable variety of surficial features not previously known from modern fans, but most side-looking systems do not provide a measure of the water depth; thus, only the plan shape is determined and not the associated relief. Without better knowledge of the actual vertical relief and of the type of sediment associated with the relief, it is difficult to use the side-looking sonar data from modern fans to help those working on outcrops by defining specific features to look for in vertical sections of ancient deposits.

NEW APPROACHES

Variations in the interpretation of deep-water fans of the kind noted above basically result from differences in the (1) types of observations used to map the deposits, (2) physical and temporal scales of features, and (3) characteristics of the basins containing the turbidite systems (Mutti and Normark, 1987, in press). Thus, it is not surprising that models derived from the separate "disciplines" lack general applicability when these differences are not taken into account.

Figure 3 shows the range of physical scales (horizontal dimension only) of the components of turbidite systems and of the types of observations commonly used to map turbidite systems. The key points to note are that the smallest features resolvable on modern deep-water fans and within deeply buried fan systems in continental-margin basins using standard shipboard seismic-reflection profiles could be recognized only in fairly impressive outcrops of ancient turbidites, where exposed beds could be traced over several kilometers. The limits on resolution obtainable with seismic-stratigraphic data nearly preclude the recognition of individual depositional lobe features unless they exceed several tens of meters in thickness. Thus, there are many gaps in the scale resolved and type of observations used to map turbidite systems.

The vertical scale in figure 3 schematically shows the general increase in the complexity and volume of turbidite systems as the time available for deposition in the basin increases. Thus, techniques appropriate for the study of depositional processes (at the scale of individual beds and elements; fig. 3) are quite different from those

that might yield basin history and an evaluation of the potential for petroleum reserves.

Comprehensive process or stratigraphic models for deep-water fans must be based on a combination of morphologic, sedimentologic, and structural/stratigraphic criteria; that is, they must be able to incorporate all types of observations. This can be done if similarly formed features of the same general scale are correctly identified. Rather than looking for general similarities among different fans to develop a model synthesizing sets of characters, Mutti and Normark (1987, in press) suggested that it is time to focus on key depositional and erosional features that characterize most turbidite systems. They identified a limited number of fan elements in terms that allow their recognition from outcrop, morphologic, or reflection-profile data; these elements are not strictly equivalent to the "architectural elements" of Miall (1985) because of the need to allow their distinction using widely varying techniques of observation (fig. 3). The basic elements include channels and channel-fill sequences, overbank deposits, lobe deposits, and characteristic erosional features, for example, scours, which are characteristic of the channel-lobe transition zone and large-scale shelf-edge/upper-slope failures (Mutti and Normark, 1987, in press).

The size and shape of the basin, together with the volume and grain-size distribution of the sediment supplied to the basin, are important factors in controlling the scale of the elements developed within any given turbidite system. Many comparisons of submarine fans have not considered the effects of the basin itself on controlling the growth pattern of the deposit.

Most turbidite systems described through outcrop mapping and borehole sampling are from basins formed on continental crust. The best known examples are from active margin environments where the basin shape, size, and longevity are controlled by syndepositional tectonism. Many of these basins are relatively narrow, elongate

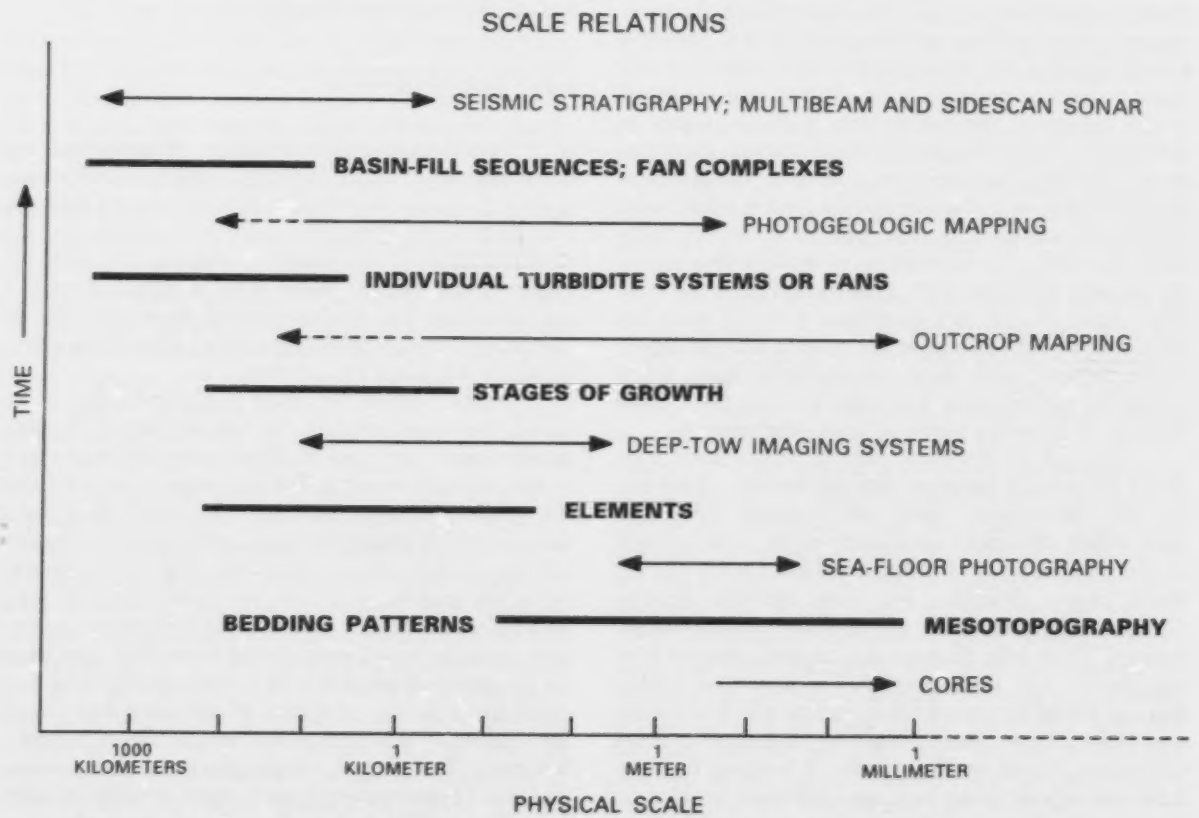

Figure 3. Relation in horizontal scale between observational techniques (light horizontal lines with arrows) used to map turbidite systems and components that compose such systems (heavy lines). Arrowheads indicate that scale range can be longer in special circumstances; for example, core samples can provide data at much smaller scale through the use of microscopic examination, and outcrops of exceptional length (>50 km) are known but not common. Vertical scale (schematic only) shows time element related to components of a turbidite system. Adapted from figures 1 and 2 in Mutti and Normark (1987), who defined elements and stages of turbidite systems.

troughs that provide a strong control on the turbidity currents bringing sediment to the basin. Much of the available observations on modern fans, however, comes from deposits formed on oceanic crust; the largest modern fans are fed by large rivers crossing passive margins where there is little tectonic activity to disturb the growth of the fan (Bouma and others, 1985). Fans formed on oceanic crust are deposited from turbidity currents that are able to spread over large areas of the sea floor as deposition buries the local relief. Thus, the shape, internal structure, and distribution of coarse-grained sediment can be substantially different between turbidite systems in active marginal basins and those on deep-ocean crust along passive margins. Comparison of submarine fan elements of similar size and from the same type of basin can be the first step in determining the main controls on deep-water siliciclastic turbidite deposition. If we understand these controls for turbidite systems from a sufficient range in size and basin characteristics, it should eventually be possible to develop depositional models of general applicability.

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Porosity

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Porosity is a volumetric measure of the interstices (pores) through which basin fluids must migrate and in which hydrocarbons are reservoired and is thus an important element of all petroleum systems. Porosity is defined as the percentage of the bulk volume of a rock that is occupied by interstices. Primary porosity refers to the original porosity still remaining. Secondary porosity refers to porosity developed during burial by chemical processes and fracturing. Effective porosity includes only those pores that are interconnected.

The common methods of porosity measurement reflect three scales of investigation: point counting describes thin sections with a thickness of 30 micrometers; laboratory methods involving the displacement or injection of inert fluids (typically mercury or helium) use core plugs with volumes of roughly 10 cm^3; and conventional wire-line logs sample rock volumes on the order of 1 m^3.

The measurement scale of porosity determinations is orders of magnitude smaller than that of petroleum systems. Furthermore, the lateral spacing of porosity measurements (and frequently the vertical spacing as well) is typically much larger than the scale of geologic heterogeneity. Therefore, in order to characterize the porosity distribution within a petroleum system, one must usually extrapolate from available porosity data according to some predictive model.

At the time of deposition, detrital sediments have porosities of 40 percent or more (Schmoker and Hester, 1986; Houseknecht, 1987; references cited therein). In the subsurface, however, porosities tend to be much lower. The dominant trend of porosity evolution in the subsurface is that of porosity destruction, as processes act to increase the thermodynamic stability of the system (Choquette and Pray, 1970; Baker and others, 1980).

The inexorable decrease of porosity during burial is not uniform, well-ordered, or easily comprehended, and therein lies the impetus for research. The primary thrust of current research related to porosity is not directed at measurement techniques but rather at the development of models for porosity variability in the subsurface.

Efforts to quantify subsurface porosity-affecting processes have included classical mathematical analyses (Durney, 1972; Elliott, 1973; de Boer, 1977; Tada and others, 1987), laboratory experiments (Sprunt and Nur, 1976; de Boer and others, 1977; Baker and others, 1980), computer modeling of subsurface chemical systems (summarized by Meshri, 1987), and the application of fractal geometry to pore systems (Krohn, 1988). Porosity is a particularly intractable parameter because it represents the space between minerals under investigation rather than the minerals themselves. The relations between matrix change and resulting porosity modification are complex and depend on a number of factors including grain shape and packing as well as on the value of porosity itself (Rittenhouse, 1971; Manus and Coogan, 1974; Mitra and Beard, 1980).

The progress being made in mathematical, experimental, and chemical studies of processes affecting subsurface porosity is substantial. Nevertheless, the quantitative evaluation of reservoir properties using these approaches is as yet beyond reach. Porosity change with burial must still be considered on a largely empirical basis.

Processes of mechanical compaction, chemical compaction, cementation, and dissolution all play significant roles in the evolution of subsurface porosity. Mechanical compaction reduces porosity by reorientation and fracture of grains and by ductile deformation of grains and matrix. Chemical compaction results in closer grain spacing due to the dissolution of grains at points of contact. Cementation occludes pores by the precipitation of authigenic minerals. Dissolution creates secondary pores by the chemical removal of framework grains or cement. (Dissolved material may be reprecipitated nearby, so that the development of secondary pores does not necessarily increase overall porosity.)

These four basic porosity-affecting processes are modified and controlled by a host of geologic factors. A partial list includes depositional environment, lithology, petrographic characteristics, patterns of meteoric-water circulation, chemistry of basin brines, presence of hydrocarbons, overpressuring, and proximity to fluid conduits such as faults and unconformities.

A large literature has accumulated empirically describing processes affecting subsurface porosity evolution and the modifying effects upon these processes of geologic factors such as those just listed. Significant research along these lines is continuing, as evidenced by numerous recent publications (for example, McDonald and Surdam, 1984; Scholle and Halley, 1985; Humphrey and others, 1986; Porter and James, 1986; Giles, 1987;

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Houseknecht, 1987, 1988; McBride and others, 1987; Scherer, 1987; Tada and others, 1987; Dutton and Land, 1988; Pittman, 1988; Shanmugam and Higgins, 1988; Wilson and McBride, 1988; Surdam and others, 1989).

As suggested by the preceding discussion, any viable predictive model for porosity variability in the subsurface must take into account processes as modified by geologic factors. That is, predictive porosity models must recognize individual diagenetic facies.

In addition, predictive models must also take rates of processes into account, in order to assess porosity change through time and burial within a given diagenetic facies. A common approach to this problem, and one that has been used repeatedly over the years, is to predict porosity change by correlating porosity to burial depth (for example, Athy, 1930; Maxwell, 1964; Baldwin and Butler, 1985). Depth can be accurately measured, and porosity-depth plots are of practical value for porosity prediction in some circumstances.

Depth, however, is a position coordinate that only specifies present-day location. As such, depth is not a causal variable and can be a poor indicator of the rates of processes that have acted upon a formation through time. If a region of interest is expanded to encompass more than a homogeneous thermal regime or a uniform burial history, porosity-depth plots lose their predictive value.

In the final analysis, processes of porosity change in the subsurface are influenced by time and temperature; time-temperature exposure (thermal maturity) is the relevant parameter for subsurface reaction kinetics (Siever, 1983). Plots of porosity versus thermal maturity (as opposed to depth), which typically show a power-function relationship, thus offer an alternative approach to the prediction of porosity change within a given facies (Schmoker, 1984; Schmoker and Gautier, 1988).

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Clays

By Richard M. Pollastro[1]

Over the past few decades there has been an increased interest in the study of clay and clay minerals as applied to petroleum geology. Much of this interest has been generated because clay minerals can be beneficial; they are useful as potential exploration tools for understanding basin, source-rock, and reservoir histories. In contrast, it is almost a necessity to identify the type and nature of the clay in a potential reservoir rock to avoid serious problems during the production and recovery of hydrocarbons. It is the purpose of this report, however, to address the application of clays in petroleum studies with particular attention to specific clay methods that aid in evaluating the thermal history of sedimentary basins. In terms of the petroleum system, these methods are extremely useful in assessing the thermal history of a petroleum source rock.

Prior to about 1970, a gap existed in the clay science literature addressing the problems and applications of clays in petroleum geology. The possible role of clays in the search for oil was first addressed by Weaver (1960). However, not until the 1970's and 1980's, which I refer to as the "decades of diagenesis," was there significant interest and recognition in clay minerals as related to petroleum geology. During the past decade, however, research groups, conferences, and symposia addressing clays and hydrocarbons have resulted in special volumes and journal issues dedicated almost exclusively to the subject.

The earliest of these volumes containing several articles that described and illustrated the significance of clays in petroleum applications was *Aspects of Diagenesis*, edited by Scholle and Schluger (1979); a much less visible publication entitled *Geothermal Alteration of Clay Minerals and Shales: Diagenesis*, by Weaver (1979), also had considerable impact. Shortly thereafter, a short course sponsored by the Mineralogical Association of Canada resulted in a relatively informal publication entitled *Clays and the Resource Geologist*, edited by F.J. Longstaffe (1981). Special issues of *Clays and Clay Minerals* (1986a,b), both the "Clays in the Petroleum Industry Issue" (v. 34, no. 2) and "John Hower Memorial Issue" (v. 34, no. 4), contain numerous method and case history articles. Most recently, short course notes entitled *Clay Minerals for Petroleum Geologists and Engineers*, by E. Eslinger and D.R. Pevear (1988), provide an excellent overview of theory, interpretation, and case histories.

The most promising clay methods used in petroleum geology are those involving the application of clay diagenesis to the thermal and burial history of sedimentary rocks and basins. These methods can therefore also be applied to studies addressing the maturation, generation, and migration of hydrocarbons. All of the applications mentioned above involve the concepts of shale diagenesis that were first described in detail from studies of buried shale sequences in the Gulf Coast (Powers, 1957; Burst, 1959; Perry and Hower, 1970; Weaver and Beck, 1971; Hower and others, 1976). The most important diagenetic clay reaction in shales is the progressive transformation of smectite to illite by way of a series of mixed-layer illite/smectite (I/S) intermediates; this particular reaction series is commonly referred to as smectite diagenesis. Presently, there is a major controversy in clay science over the true crystallographic nature of material identified as I/S by X-ray powder diffraction (XRD). However, whether these changes are interpreted by the mixed-layer (Markovian) model (MacEwan, 1956, 1958; Reynolds, 1980) or the fundamental particle (Nadeau and others, 1984a,b) concepts, the reaction results in a progressive and irreversible increase in illite and corresponding decrease in expandability (commonly interpreted as smectite).

Recognition of smectite diagenesis is based mainly on the interpretation of XRD profiles. Interpretations of the changes in XRD profiles of I/S were first defined in detail by Reynolds and Hower (1970) who compared XRD profiles of natural materials to those calculated by computer. Their methods defined three basic, naturally occurring forms of I/S ordering: random (R=0) ordering, short-range or allevardite-like (R=1) ordering, and long-range or Kalkberg-like ($R \geq 3$) ordering. A method to calculate the approximate percentages of illite and smectite (expandable) layers in the mixed-layer phase also was proposed. Subsequently, numerous changes and updates in the modeling program have been made by Robert C. Reynolds Jr.; the latest version of the program, entitled NEWMOD, is available from Reynolds (Department of Earth Sciences, Dartmouth College, Hanover, NH 03755). In addition, several other methods have been described in the literature after the work of Reynolds and Hower for interpreting XRD profiles of I/S (Schultz, 1978; Srodon, 1980; Srodon and Eberl, 1984; Inoue and others, 1989).

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The most useful clay method applied to petroleum geology studies is clay mineral geothermometry. Concepts and models of clay geothermometry in diagenetic settings were first proposed by Hoffman and Hower (1979) and Weaver (1979). Changes in the I/S "phase" interpreted from XRD profiles show consistent relations with depth which, in fact, are related primarily to changes in temperature due to burial. Similar clay/temperature relations have been demonstrated for hydrothermal fluid systems and low-grade contact metamorphic situations. However, temperatures for changes in I/S phase differ in hydrothermal systems as compared to those temperatures for similar changes in I/S from progressive burial settings. These changes in I/S, therefore, are reliable maximum recording geothermometers provided that the proper temperature model is used (Pytte and Reynolds, 1989; Pollastro, 1989). During the last decade, numerous case history studies have applied and tested I/S clay models in diagenetic and hydrothermal settings worldwide. Other clay minerals that have been formed, destroyed, or changed during diagenesis, as well as I/S, also give reliable temperatures. No other clay minerals, however, have been studied or tested to the extent of the I/S series.

The most important change in I/S in relation to hydrocarbons is the conversion from random I/S (R=0) to ordered I/S (R=1). In samples from well profiles, the primary criterion for recognition of this conversion is the absence, or disappearance in downhole samples, of the 17-angstrom glycol *001* reflection on XRD patterns. The immediate change is recognized by the presence of a lesser expandable phase with smaller d-spacing (usually about 13 to 14 angstroms upon glycol solvation). However, the *001* glycol reflection of I/S with R≥1 shifts between 10 and 14 angstroms, depending upon specific composition and degree of ordering (Reynolds and Hower, 1970). If the actual change in the I/S reflections on XRD profiles cannot be recognized from random sampling or sample profiles, however, sufficient evidence must be established from control samples that a precursor 17-angstrom glycol, random-ordered phase existed before the I/S can be used as an absolute geothermometer. It is critical, therefore, to establish original compositions of these clays because detrital I/S may have undergone extensive illitization during a previous cycle (Pollastro and Scholle, 1986).

In burial diagenetic settings, this major change in I/S (R=0 to R=1) occurs in the temperature range of about 100 to 110 °C (Hoffman and Hower, 1979) and is roughly coincident with the onset of oil generation in rocks of Tertiary through Cretaceous age. In relatively short-lived (commonly <2 m.y.) geothermal systems, however, the temperature of this particular I/S change is about 130 to 140 °C. I/S with R=1 ordering, typically with 60 to 80 percent illite layers, is thermally stable between 100 and 175 °C. This temperature range is roughly coincident with the "oil window." Therefore, the simplest application of clays in burial diagenetic settings is to record the 100 to 110 °C isotherm using the R=0 to R=1 transition (Pollastro and Scholle, 1986; Pollastro and Schmoker, 1988), thereby providing an index of thermal maturity relative to hydrocarbon generation (Foscolos and Powell, 1980; Pollastro and Scholle, 1986). The method also has been used in modeling the thermal history of sedimentary basins (Bethke and others, 1988; Hagen and Surdam, 1989). This method is particularly valuable for samples lacking either vitrinite or other indicators from which the maturity level can be estimated directly. For example, the presence of a distinct 17-angstrom glycol XRD peak suggests that the rock is immature or marginally mature with respect to oil generation. Temperatures determined for this change in I/S phase shows excellent agreement when compared to temperatures calculated from mean vitrinite reflectance and "T_{max}" (Pevear and others, 1980; Burtner and Warner, 1986; Pollastro and Barker, 1986; Glassman and others, 1989, among others). Other studies have related this change in I/S to particular stages of oil generation (Weaver, 1979; Pollastro and Schmoker, 1988).

Clay geothermometry from changes in I/S observed on XRD profiles is also reliable at temperatures higher than the change from R=0 to R=1. The conversion from R=1 to R≥3 ordering occurs at about 175–180 °C (Hoffman and Hower, 1979) and can document the upper limit of oil generation for a particular potential source rock. A sample containing only R≥3 I/S would, therefore, be overmature with respect to oil generation and only would have potential to generate thermal methane. At temperatures exceeding those of the I/S transformation series, a different method in clay geothermometry is widely used. This method involves measurement on XRD profiles of peak width or a height-to-width ratio of the illite *001* (10-angstrom) reflection. Various forms of this method are referred to as "illite crystallinity," "crystallinity index," "Kubler index," "Weaver index," and "sharpness ratio" (Weaver, 1960, 1979; Kubler, 1964; Heroux and others, 1979). Although illite crystallinity correlates with vitrinite reflectance, the method is commonly applicable to levels of thermal maturity exceeding those for the generation of hydrocarbons.

Smectite diagenesis, specifically the major I/S change at 100 to 110 °C in progressive burial settings, has several other implications in petroleum geology. However, many of these implications are unclear and will require further research. For example, Surdam and others (1984, 1989) and Surdam and Crossey (1985) have used the coincidence in time and temperature of organic and clay reactions for characterizing the diagenesis of reservoir/source rock systems. The major I/S reaction at 100 to 110 °C is coincident with temperatures of organic acid maxima (80–120 °C). These authors suggested that

mineral oxidants and dehydration reactions involved in the conversion of smectite to illite contribute to creating optimum diagenetic conditions for maximizing porosity preservation or enhancement in sandstone reservoirs. In contrast, many other authors have addressed smectite diagenesis as a contributor to reservoir cementation (Towe, 1962; Boles and Franks, 1979; McHargue and Price, 1982). Others suggest that the diagenetic transformation of smectite to illite results in increased catalytic activity that promotes the low-temperature transformation of organic matter into liquid and gaseous hydrocarbons (Johns, 1979; 1981; Johns and McKallip, 1989). Smectite diagenesis or specific changes in I/S have also been correlated to expulsion or migration of hydrocarbons and zones of abnormal geopressures (Powers, 1967; Burst, 1969; Bruce, 1984; Colton-Bradley, 1987; Shaw and Primmer, 1989).

In summary, clay minerals are useful tools in understanding both the depositional and diagenetic settings of sedimentary rocks. In particular, the major clay reaction in buried sedimentary rocks, the conversion of smectite to illite through I/S intermediates, is an excellent maximum recording geothermometer. Methods of clay geothermometry, therefore, can greatly assist in evaluating the thermal history of a sedimentary basin. Specific clay geothermometers are approximately coincident with temperatures for hydrocarbon "windows." In a petroleum system, therefore, clays are useful in determining the thermal history of source rocks.

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Fission-Track Analysis in Petroleum Basins

By Nancy D. Naeser[1]

THE FISSION-TRACK METHOD

Fission tracks are zones of intense damage formed when fission fragments travel through a solid. Several naturally occurring isotopes fission spontaneously, but only ^{238}U has a sufficiently short fission half-life (9.9×10^{15} yr) to produce significant numbers of tracks over times of geologic interest (Fleischer and others, 1975).

A number of common minerals contain trace amounts of uranium. Because ^{238}U fissions spontaneously at a known rate, fission tracks can be used to date these minerals. An age can be calculated by determining the number of spontaneous tracks intersecting a polished surface of the mineral and the amount of uranium that produced those tracks. The two minerals most commonly dated by the fission-track method are apatite and zircon. The techniques used in dating have been developed by physicists and geologists since the early 1960's (Fleischer and others, 1975; C.W. Naeser, 1976, 1979a; N.D. Naeser and others, 1989b).

If a mineral containing fission tracks is heated to a high enough temperature, the damage zone undergoes progressive shortening and ultimately disappears, leading to a reduction in the number of observable tracks and thus an anomalously young fission-track age. Different minerals undergo this "annealing" over different temperature ranges. The range for any given mineral depends on the duration of heating: the longer the mineral is heated, the lower the temperature required to anneal its tracks.

More research has been devoted to determining the annealing kinetics of apatite than any other mineral. Data have been obtained both from laboratory heating experiments (for example, C.W. Naeser and Faul, 1969; Märk and others, 1973; Zimmermann and Gaines, 1978; Crowley, 1985; Green and others, 1985, 1986; Crowley and Cameron, 1987, in press; Laslett and others, 1987; Crowley and others, 1988; Duddy and others, 1988; Green, 1988; Hughes and others, 1988) and by observing the annealing behavior of apatite in drill holes in areas where the thermal history of the rocks is reasonably well known (C.W. Naeser, 1979a, 1981; Gleadow and Duddy, 1981; N.D. Naeser and others, 1987a, 1989a).

Ongoing research continues to more accurately define apatite annealing kinetics, clarify the response of apatite track lengths to annealing (particularly in detrital suites derived from a number of parent rocks of different age and thermal history), and improve the predictive capabilities of apatite annealing models. One topic that has received considerable attention in recent years is the effect of chemical composition on annealing temperatures of apatite. It now appears that the annealing susceptibilities of F-, Sr-F-, and OH- apatite are so similar that all can probably be approximated by F-apatite data. Chlorapatite, however, is significantly more resistant to annealing; at fixed heating times in the laboratory, it anneals at temperatures up to 30 °C higher than other apatite varieties (Crowley and Cameron, 1987; Crowley and others, 1988; Hughes and others, 1988). Similiar variation in annealing temperatures related to Cl content is observed in drill-hole samples from the Otway basin, Australia (Green and others, 1985, 1989). Available information indicates that, in contrast to the Otway Basin, apatite suites are typically dominated by fluorapatite with insignificant chlorine (for example, Berry and Mason, 1959; Deer and others, 1962; N.D. Naeser and others, 1989a) and can reasonably be interpreted using fluorapatite annealing temperatures. Nevertheless, until the effects of composition on annealing temperatures are fully resolved, this topic will undoubtedly continue to be investigated, and it should be considered when interpreting apatite fission-track data.

The most complete set of empirically derived annealing temperatures presently available (C.W. Naeser, 1981) was determined on fluorapatite (K.D. Crowley, written communication, 1988). These data indicate that apatite is effectively totally annealed (yields a zero age) at temperatures that range from about 105 °C for relatively long-term heating of about 100 million years duration to 150 °C for about 100,000 years.

Annealing temperatures for zircon are not as well known as for apatite, but limited data show that they are higher and are probably in the range of 160 to 250 °C for heating over periods of more than 1 million years (for example, Harrison and others, 1979; C.W. Naeser, 1979a; Zeitler, 1985; Hurford, 1986).

BASIN ANALYSIS

Fission tracks in apatite and zircon are used in a wide range of studies in basin analysis (reviewed in N.D. Naeser and others, 1989b). The annealing of fission

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tracks, and the resulting effect on fission-track age and track lengths, particularly in apatite, can be used to reconstruct the thermal history of basins, from the deposition and burial of sediments through subsequent cooling related to uplift and erosion. Annealing can also be used to define more localized temperature anomalies, such as those related to intrusions and to the passage of high-temperature fluids through a basin (C.W. Naeser, 1979b; Gleadow and others, 1983, 1986a, 1986b; Green and others, 1989; N.D. Naeser and others, 1989b). The first study using fission tracks to reconstruct the thermal history of a basin appeared only 10 years ago, but the method has now been used in basins throughout the world (for example, Briggs and others, 1979, 1981a, 1981b; Duddy and Gleadow, 1982, 1985; Gleadow and others, 1983; Lakatos and Miller, 1983; Gleadow and Duddy, 1984; N.D. Naeser, 1984, 1986, in press; Johnsson, 1985, 1986; Giegengack and others, 1986; Marshallsea, 1986; Miller and others, 1986; Duddy and others, 1987; N.D. Naeser and others, 1987a, 1989a, 1989b, in press; Dumitru, 1988, 1989; Feinstein and others, 1989; Green and others, 1989). Fission tracks in apatite and zircon are attractive for studying the thermal history of basins because they provide both *temperature* and *time* information over a temperature range that coincides with hydrocarbon generation temperatures (Hood and others, 1975; Waples, 1980; N.D. Naeser and others, 1989b), temperatures recorded in the paleothermal anomalies associated with some mineral deposits (C.W. Naeser and others, 1980; Cunningham and Barton, 1984; C.W. Naeser and Cunningham, 1984; Beaty and others, 1988), and temperatures associated with a number of other low- to moderate-temperature processes in basins such as, clay diagenesis and conodont color alteration.

Typically, information on thermal history of basins is provided by apatite because most rocks sampled in basins have not been heated to temperatures sufficiently high to anneal zircon. The presence of unannealed zircon does, however, set approximate limits on maximum paleotemperatures, and the ages of individual unannealed zircon grains provide data on the provenance of sediments that may be difficult to obtain by other methods. For example, within a detrital grain suite it may be possible to correlate individual age populations to probable parent rocks in order to delineate sediment transport patterns in a basin (Zeitler and others, 1982, 1986; Hurford and others, 1984; Johnson, 1984; Yim and others, 1985; Baldwin and others, 1986). Changes in the age populations observed in a series of samples collected through a stratigraphic section in a basin can be used to reconstruct changes in sedimentation patterns, to define input from different source areas, and to reconstruct the uplift and erosion history of the parent rocks (Zeitler and others, 1982, 1986; N.D. Naeser and others, 1987b; Cerveny and others, 1988).

Zircon has also been used extensively to date volcanic ashes (and their altered equivalents, bentonites and tonsteins) (reviewed in C.W. Naeser and N.D. Naeser, 1988). These units form widespread marker horizons that can be valuable for establishing correlation and chronology within sedimentary sequences.

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Geothermics Applied to the Reconstruction of Subsurface Temperatures

By Charles E. Barker[1]

INTRODUCTION

Determination of accurate subsurface temperatures is a crucial element of petroleum geology. Yet accurate measurement has proven to be an imprecise, error-prone procedure whether in the simpler case of present-day formation temperature, or the more difficult evaluation of paleotemperature. This paper overviews methods of determining both modern and ancient subsurface temperatures. The treatment is not comprehensive, and emphasizes the most recent literature and techniques that I have found useful. Only relevant summary papers are cited in the text. The methodology discussion is supplemented by an extended bibliography. If the subject of the reference is not sufficiently clear in the title, the citation is annotated.

CORRECTION OF TEMPERATURE MEASUREMENTS

Direct determination of accurate present-day formation temperature in wells requires thermal equilibrium before measurement. A rule of thumb is that it requires about the same amount of time for a well to recover from drilling fluid circulation effects as it took to drill the well (Bullard, 1947). However, usually this length of reequilibration time is not available before a bottom hole temperature (BHT) is measured, usually within a few hours of drilling. Most BHT's do not represent true (equilibrium) formation temperature and the measurement must be corrected.

Statistical Correction Methods

The information necessary to calculate a correction to logged temperature to equilibrium formation temperature is often not included, or is inaccurate, in the well logging reports (Carstens and Finstad, 1981; Catala, 1984). Thus, accurate correction of BHT is difficult. For all of the uncertainty in determining the true formation temperature, it is reasonable to make a BHT correction because we do know that equilibrium formation temperature is higher than an unequilibrated BHT. The simplest correction is to compile producing well temperatures (or drill stem test information) and the corresponding BHT at reservoir depth for computation of a correction curve. The correction is made by adding the difference between the higher formation temperature and the lower BHT data calculated at the bottom hole depth. The quality of correction improves with the type of data available, with the best case being careful measurements repeated over time until temperature no longer changes. A widely used statistical correction is the AAPG method (AAPG, 1976; see also Scott, 1982). The AAPG correction was developed in and applied to wide geographic areas and has proved inaccurate in parts of some basins. The statistical approach, in general, is imprecise as shown by a wide data scatter about the correction curve generated for a single basin (for example, Chueng, 1979). Although imprecise, the statistical method in many cases is the only correction possible.

Empirical Correction Methods

Commonly used empirical techniques are (1) the Horner plot (limits of application in Dowdle and Cobb, 1975, and (2) the Middleton (1979) curve-matching method. Leblanc and others (1982) suggested use of the Horner plot when the mud equilibration time to the BHT measurement is known, and the curve-matching technique when it is not known.

Present Temperature-Depth Reconstruction

A geothermal gradient is calculated by interpolation using mean annual surface temperature to the depth of the corrected BHT. This linear approximation can be highly inaccurate because the vertical and lateral temperature profile can change with lithology (thermal conductivity), different fluids filling the pores, subsurface fluid flow, and so forth. This constructed geothermal gradient gives no information about paleotemperature. Many workers assume, in the absence of compelling information to the contrary, that present measurements can be extended into the past. Such an assumption often cannot be contradicted with other geologic information, and it is a useful first approximation.

[1]U.S. Geological Survey, Denver, Colo.

In the absence of detailed paleotemperature evidence, the calculated geothermal gradient is often assumed to remain constant without regard to temporal heat-flow variation and diagenesis (primarily porosity loss) or change in lithology. Thus, a detailed geologic analysis is unfortunately reduced to time-temperature data by simplification of the geothermal gradient into a linear form and ignoring its possible temporal change. However, gaps in the geologic record, and the data quality and quantity available, often will not permit a more sophisticated approach. An accurate time-temperature determination is crucial to Lopatin thermal maturity (TTI) estimates because it is sensitive to small changes in subsurface temperature; an increase of just 10 °C increases TTI by 100 percent.

THERMAL HISTORY RECONSTRUCTION

Paleotemperature reconstruction requires geologic data to document the temporal change in (1) the values of geothermal gradient, surface temperature, and burial depth history or (2) heat flow and thermal conductivity. These data are difficult to reconstruct because the temperature regime has often changed, and burial history may be altered or obliterated by compaction, erosion, and structural complexities. Further, present-day measurements should be calculated to a decompacted value. For example, thermal conductivity is dependent in part on the porosity and the fluid filling it. So contemporary thermal conductivity measurements must be adjusted (lowered) to the former (higher) levels of porosity (Lewis and Rose, 1970) and must consider in some cases the displacement of pore water by oil and(or) gas.

A paleosurface temperature is required to estimate subsurface temperature if only a paleogeothermal gradient is available. Surface temperature estimates can be made using four methods: (1) fossil evidence for paleoclimate (Savin, 1977); (2) reconstruction of paleolatitude by use of continental drift models (Weijermars, 1989; Dagger, 1989) and present models of broad latitudinal and elevation control of mean surface temperature[2]; (3) contemporary measurements before apparent perturbation by the greenhouse effect (Darton, 1913); and (4) average near-surface water temperature (Blakey, 1966).

[2]The present surface temperature of the Earth as a function of north or south latitude (lat) is $T=27.6-(0.04\ lat)-(0.006\ lat^3)$ ($r^2=0.99$; computed using data from the U.S. Weather Bureau). Note that the average global temperature is now 15 °C, but in the past has decreased to as low as 10 °C in the coldest glacial periods and has been as high as 22 °C, so this function must be carefully applied. Also, an elevation correction may have to be applied.

Burial Depth History

Burial depth reconstruction is usually based on a simple layer-cake concept of sediment accumulation. Another approach is to model the rate of sedimentation through time. Burial curves should be corrected for compaction (Perrier and Quiblier, 1974) to improve accuracy in paleodepth assessment. Paleotemperature history is computed using burial depth through time and the estimated geothermal gradients (Waples, 1985).

Erosion Estimates

The simplest method for determining depth of erosion is by stratigraphic projection of formation thickness from a related uneroded section to the eroded one, or measure the sediment thickness eroded from the crest of folded beds (see discussion in Magara, 1986). Geologic or geochemical parameters that vary regularly with depth and do not significantly change during exhumation can also indicate depth of erosion (gradient method). For example, using thermal maturation data, the slope and intercept of the vitrinite reflectance-depth profile are measured. A semilogarithmic plot of vitrinite reflectance and depth straightens the maturation curve projection to the vitrinite reflectance estimate at the pre-existing ground surface (Dow, 1977). Projecting the regression curve to a paleosurface vitrinite reflectance value of 0.2 percent indicates an eroded thickness in good agreement with other geologic data (Nuccio and Barker, 1989). The gradient method must be modified to work thermal maturity data across with buried erosional surfaces (Katz and others, 1988).

Thermal History Reconstruction

Once surface temperature, paleodepth, and paleotemperature estimates are reconstructed, a geothermal gradient is calculated by a procedure similar to that used with BHT data. As for present-day temperature data, linear interpolation in a heterogeneous sediment pile makes many assumptions that are not very robust, but often it is the only method available. The thermal history (temperature at some point as a function of geologic time) is calculated by using paleogeothermal gradients reconstructed for each time period and calculating temperature based on surface temperature and paleodepth from the depth-time curve.

Paleotemperature from Thermal Conductivity and Heat Flow

Fourier's law states that the heat flow is directly proportional to thermal conductivity of the strata and the geothermal gradient. The temperature at the bottom of a sediment package is determined by using Fourier's law

relating the temperature at the top of the unit (initially the average surface temperature), its thermal conductivity, and local terrestrial heat flow[3] (Gretener, 1981; Buntebarth, 1984). A modification of this technique is the thermal resistance (Bullard) method of computing subsurface temperature (Andrews-Speed and others, 1984). Contemporary terrestrial heat-flow measurements throughout the world are available from regional contour maps. The thermal conductivity of a rock unit is estimated using a weighted average proportioned to the abundance and thermal conductivity of each lithology present (as suggested by Reiter and Tovar, 1982). An important consideration in the thermal conductivity computation, because it is a bulk property, is the porosity and pore fluid composition. For example, experiments by Woodside and Messmer (1961) and theoretical modeling (Lewis and Rose, 1970; Buntebarth, 1984) show that filling pores with oil and(or) gas can cause major reduction of bulk-rock thermal conductivity.

Direct Geothermometry

Geothermometers based on inorganic materials (fluid inclusions, diagenetic mineral assemblages, illite crystallinity, isotopes, and so forth) and organic matter (rank indices of kerogen or coal) have been calibrated to burial temperature (Frey, 1987). The limitation of these geothermometers is that the thermal history must be recorded in the rocks. Thermal events can be difficult to record in sedimentary systems because of the slowness of low-temperature equilibration reactions. The short-term nature of some thermal events may also preclude them from leaving an imprint on the rock. These problems notwithstanding, direct geothermometry has proved to be a useful tool in subsurface paleotemperature studies.

DISCUSSION

Thermal history reconstructions are often fragile interpretations of geologic semi-fact, because they are based on many assumptions and extrapolations (the proverbial house of cards). The validity of these reconstructions should be evaluated on a case by case basis. The best check is to make both direct and indirect estimates of the thermal history using all possible methods and data.

[3]Conversion factors: Geothermal gradient: °C/km=18.23 °F/100 ft. Heat Flow: HFU=1 microcal/cm^2-s=41.8 mW/m^2. Thermal conductivity: W/m-°C=2.4 mcal/cm-s-°C.

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Role of Kinetic Modeling in Petroleum Exploration

By Jerry L. Clayton[1]

Although a few investigators have suggested that petroleum may be derived from abiological sources (Gold and Sofer, 1980; Porfir'ev, 1974), the present consensus view is that petroleum originates from thermal transformation of organic matter contained in sedimentary rocks. Some of the organic-solvent-soluble components (bitumen, lipids) contained in sedimentary organic matter may undergo only minor diagenetic alteration during burial heating, but most of the organic matter deposited in fine-grained rocks is contained in the high-molecular-weight insoluble fraction (kerogen). Kerogen decomposes during burial heating over geologic time to generate petroleum. Petroleum generated by this process consists mostly of products from the thermal transformation of kerogen with secondary amounts of lipid materials inherited directly from sedimentary organic matter without going through the kerogen intermediate step.

The main role of kinetic modeling in exploration is to reduce risk by predicting how much oil or gas has been generated in a play where direct geochemical measurements are limited or nonexistent because of lack of previous drilling or geochemical sampling. This may include undrilled basins or parts of basins, or may be deep plays in basins where only shallow wells had been drilled previously. The strategy used in applying kinetic models to exploration is to integrate the kinetics of hydrocarbon generation with the burial history (temperature history) of a source rock of interest to predict not only the type (oil or gas) and amount of hydrocarbons generated, but also the timing of generation and expulsion with respect to development of secondary migration pathways and reservoirs.

Kinetic models of petroleum generation include more general considerations of organic maturation and are useful in other geological applications besides petroleum exploration. For example, if measured geochemical data from a basin are compared with kinetic models, the burial and thermal evolution of the basin can be inferred or can be constrained to fit the kinetic limitations imposed by the organic maturation model (for example, Brosse and others, 1986; Ungerer and others, 1986; Sweeney, 1989). However, modeling of kerogen decomposition may be an unnecessarily cumbersome approach to assessment of geologic processes such as burial histories. Several workers have proposed kinetic models for specific reactions where the reactants and products are thought to consist only of a few chemical species rather than the complex kerogen-petroleum system as a whole (Mackenzie and McKenzie, 1983; Mackenzie, 1984; Alexander and others, 1986). In principle, this approach has the advantage that the specific reactions are known and kinetic parameters can be estimated with a greater degree of accuracy than for kerogen decomposition, even though the reactions may not be applicable directly to the question of petroleum generation. An understanding of the kinetics of kerogen decomposition is also required for proper design and operation of oil-shale processing plants and in situ retorting methods (Campbell and others, 1978; Shih and Sohn, 1980; Braun and Burnham, 1987).

In all of the above geologic applications, the usefulness of the kinetic modeling approach is limited by (1) how well the geologic and thermal history of the basin are known and (2) how accurately the kinetic model describes the real behavior of organic matter during burial heating over geologic time. The first limitation depends entirely on how well the geology and thermal history of the subject basin are known. Limitations in geologic methods and techniques for measuring current temperatures or estimating paleotemperatures determine the accuracy of geologic and thermal data. With regard to the second factor, the validity of kinetic models, much progress has been made in recent years in our understanding of the thermal evolution of organic matter. Nevertheless, there is enough uncertainty in our knowledge of fundamentals such as the mechanism and stoichiometry of petroleum generation to introduce significant uncertainty in applications of kinetic models when insufficient geologic data are available to properly constrain the models.

A number of workers have conducted field and laboratory studies of the kinetics of petroleum generation with the goal of developing kinetic models that can be used to predict oil or gas generation for a specific basin or source rock horizon. Over the past 30 years, a number of models have been proposed. All of the models currently in widespread use are based on the Arrhenius equation, which means that oil generation depends on some combination of time and temperature; that is, thermal transformation of kerogen during burial heating over geologic time.

$$dP/dt = e^{-kt} \text{ where } k = A \exp(-E_a/RT) \quad (1)$$

[1]U.S. Geological Survey, Denver, Colo.

where

dP/dt	=	yield of product (oil or gas) with respect to time (t) for a given temperature (T)
k	=	rate of the reaction
A	=	Arrhenius constant
E_a	=	activation energy
R	=	gas constant

However, the models that have been proposed vary considerably with respect to the values for kinetic parameters (E_a, A) and the relative emphasis assigned to time or temperature as factors in petroleum generation (and thermal destruction). A historical perspective and basic explanations of the underlying theoretical principles of thermal models are given in the review by Waples (1984) and references therein.

Calibration of kinetic models is often based solely on laboratory data, especially if the objective is to evaluate the petroleum potential of a frontier area where field data are unavailable. Potential problems arising from laboratory calibrations include the fundamental question of the applicability of the Arrhenius equation over the wide range of temperatures associated with laboratory studies and petroleum generation and destruction (Burnham and others, 1989), and technical problems of laboratory measurement of kinetic parameters. Laboratory methods of obtaining kinetic parameters and potential problems are discussed by Burnham and others (1987, 1989). Detailed descriptions of methods for laboratory determination of kinetic parameters and the theoretical basis of these procedures are given by Braun and Burnham (1987), Burnham and Braun (1985), and Burnham and others (1987, 1989).

One of the earliest petroleum-generation models that enjoyed wide acceptance was that of Lopatin (1976), which became very popular following the summary by Waples (1980). The Lopatin method was used routinely in the early 1980's by many explorationists. Recently, the Lopatin method has largely been supplanted by models using more rigorous approaches based, for example, on the petroleum-generation model of Tissot and Espitalié (1975) (for example, Ungerer, 1984; Ungerer and others, 1986). Nevertheless, the Lopatin model is still used in some cases and can be a useful predictive tool if properly calibrated (Horváth and others, 1988).

Many of these more recent, mathematically rigorous models, include not only the kinetics of petroleum generation, but also more detailed treatment of the burial history of the basin under investigation. These types of models include calculation of pressure, temperature, and physical and thermal properties of the sediments as well as petroleum generation (for example, Welte and Yukler, 1981) and are really basin evolution models rather than strictly petroleum-generation models.

Development of detailed mathematical kinetic models of petroleum generation is due not only to recognized weaknesses in simpler models, but also to the availability of desktop computers with sufficient capacity to perform the necessary calculations quickly. Future research in the area of kinetic modeling of petroleum generation must include refinements in methods for obtaining thermal data for basins—both paleotemperature data and accurate determinations of present temperature conditions. The models themselves can be improved by increased understanding of kerogen structure and thermal behavior and by improvements in laboratory determination of kinetic parameters used in kinetic calculations. Parallel with the continued development of highly sophisticated chemical and computer models, training of explorationists in the applications and especially the limitations of these models must be addressed. Poor understanding of the theoretical basis of the models or the laboratory methods used to obtain input data can lead to serious misinterpretation of kinetic modeling results.

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Biological Marker Chemistry as Indicator of Depositional Environment of Source Rocks and Crude Oils

By Jerry L. Clayton[1]

The term "biological marker" or "biomarker" was first introduced in the literature by Speers and Whitehead (1969), although the idea of chemical "fossils" has been around much longer (Fox, 1944). More recently, Mackenzie (1984) defined biological markers as "any organic compound detected in the geosphere whose basic skeleton suggests an unambiguous link with a known, contemporary natural product." The operative word in this definition is "unambiguous." It is generally accepted that petroleum is formed from thermal transformation of sedimentary organic matter derived from living systems. During burial heating, sedimentary organic matter evolves from a complex mixture of a wide variety of molecules derived more or less directly from living systems to a mixture of fewer types and simpler chemical structures. Given sufficiently high temperatures over geologic time, only methane would remain. Therefore, as thermal maturation proceeds, the structural similarity between biological marker compounds in rocks or petroleum and their precursor biomolecules in living systems becomes increasingly more ambiguous. One of the main objectives of biological marker research is to recognize the link, or diagenetic pathway, between biomolecules in living systems and biological marker compounds found in rocks or oils that have undergone variable degrees of alteration during burial heating over geologic time.

The first biomarker compounds to be identified in geological materials were porphyrins, which are diagenetic products of chlorophyll (Treibs, 1934a, b, 1935a, b, 1936). Owing to the development of sensitive analytical tools, particularly gas chromatography-mass spectrometry, significant advances have been made over the past 20 years in identification of biological marker compounds in rocks and petroleum. Many studies, particularly early work, have been concerned primarily with the identification of chemical structures of biological markers in sediments and oils (for example, Han and Calvin, 1969; Balogh and others, 1973; Kimble and others, 1974; Seifert, 1975; Seifert and others, 1978; Rowland and others, 1982; Schmitter and others, 1982; Trendel and others, 1982; Ekweozor and Straus, 1983; many others). In recent years, more attention has been given to applications of biological markers in petroleum geochemistry. Comprehensive reviews of biological marker geochemistry and applications are given by Mackenzie (1984) and Johns (1986).

Biological markers are important in petroleum systems for interpretation of oil-to-oil and oil-to-source rock correlations, thermal maturation, biodegradation, and migration. The present paper summarizes applications of biological markers in interpretation of depositional environment of source rocks. This includes consideration not only of source rocks themselves but also crude oils, because the biological marker composition of oils can be used in some cases to infer the depositional setting of the parent source organic matter.

Interpretation of the depositional setting of sedimentary organic matter using biological markers can be approached in two ways. First, chemical conditions in the sedimentary environment may be inferred from which diagenetic reactions occur among numerous possible reaction pathways. For example, the ratio of pristane-to-phytane has been suggested as an indicator of the relative oxicity or anoxicity of sediments in which organic matter accumulates (Didyk and others, 1978), although recent evidence suggests that factors other than redox potential may affect the ratio (Goossens and others, 1984; ten Haven and others, 1987). Second, biological markers that are characteristic of a particular organism or a group of organisms indicate the chemistry of the depositional environment because of the ecological requirements of the contributing organisms. For example, the presence of certain isoprenoid compounds characteristic of methanogenic bacteria indicate strongly reducing conditions because methanogens are strict anaerobes, while euxinic conditions can be inferred from the presence of aryl isoprenoids, which have been suggested as indicators of green photosynthetic sulfur bacteria (Summons and Powell, 1987). Many studies of biological marker assemblages in sediments and petroleum have been aimed at interpreting the specific type of environment or overlying water column in which the sediments were deposited, such as lacustrine freshwater, freshwater brackish, saline, or hypersaline (for example, Mello and others, 1988; Brassell and others, 1988; Fu Jiamo and others, 1986; ten Haven and others, 1988; Volkman, 1988).

Biological markers can also be used to infer the biological source of the organic matter. In this case, interpretation of the organic input is the objective, rather

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than the actual paleoenvironment in which sediments were accumulating. Organic input to the sediments may be predominantly from organisms populating the sedimentary environment, in which case the approach used to interpret the paleoenvironment would lead also to an understanding of the main source input. However, in many cases nonindigenous (allochthonous) organic matter may be present in significant amounts. In this latter case, interpretation of the depositional environment requires differentiating between the biological marker components that are derived from organisms populating the sedimentary environments and those associated with allochthonous organic input. The main groups of organisms contributing organic matter to sediments are higher terrestrial plants, algae, and bacteria (Tissot and Welte, 1984). Comet and Eglinton (1987), Brassell and others (1987), and Volkman (1988) discussed biological marker assemblages that are characteristic for these three groups of organisms.

Future research in applications of biological markers for interpreting depositional environment will include continuing expansion of the inventory of biological marker compounds in living organisms, sediments, and oils. In addition, further work is needed to elucidate diagenetic and catagenetic pathways of biological marker evolution and factors which favor particular reaction pathways (such as heating rate, Eh, pH, mineral matrix, or temperature).

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Sulfur in Source Rocks and Petroleum

By Jerry L. Clayton[1]

The purpose of this report is to summarize current understanding of the geochemistry of organic sulfur compounds (OSC) in crude oil and source rocks. Sulfur is the most abundant nonhydrocarbon component in crude oil; the average sulfur content of oil is about 0.65 percent (Tissot and Welte, 1984). The range is from a few hundreths of 1 percent up to 8 percent and rarely up to 10 to 14 percent, although most crude oils contain less than 4 percent (Constantinides and Arich, 1967; Ho and others, 1974; Orr, 1978; Tissot and Welte, 1984; Bolshakov, 1986). Tissot and Welte (1984) considered 1 percent total sulfur to be the boundary between high- and low-sulfur oils. Most of the sulfur in crude oils is contained in organic compounds; secondary amounts are present as dissolved elemental sulfur or metal sulfides (Orr, 1978). OSC occur predominantly in the middle to high boiling point range in most crude oils (Sinnighe Damasté and others, 1988a).

OSC are of considerable interest to explorationists and refinery chemists for several reasons. OSC in petroleum present serious refining and environmental problems that can significantly diminish the economic value of a given petroleum deposit. Therefore, explorationists need to be able to predict the occurrence of high-sulfur crude oil with some degree of accuracy. Furthermore, sulfur compounds in crude oils occur in a wide variety of organic structures, many of which are thought to involve early diagenetic reactions of sulfur with biomolecules derived directly from organisms contributing organic matter to sediments (Sinnighe Damasté and others, 1987c) and can therefore be used for oil-source rock correlations and for interpretation of paleoenvironment of deposition of organic-rich rocks (Brassell and others, 1989; ten Haven and others, 1985, 1988; Kohnen and others, 1989; Rullkötter and others, 1989). Relative amounts of sulfur compound classes have also been used to assess the thermal maturity of oils (Ho and others, 1974), and the molecular distribution of OSC may have application in thermal maturity studies of oils or rocks (Rullkötter and Orr, 1989). Thermal requirements for breakdown of kerogen to generate oil depend partly on the distribution of sulfur bonds in the kerogen. Kerogens containing large amounts of sulfur bonds (type "II-S" kerogen) have been observed to generate oil under relatively mild thermal conditions compared to low-sulfur kerogens (Orr, 1978). Therefore, studies or models of oil generation must consider the effects of sulfur on kinetics of kerogen breakdown.

Figure 4 gives the chemical structures of the main types of OSC found in the geosphere to date. The relative importance of the different sulfur structural types varies markedly among different oils in response to a variety of factors such as the organic source, thermal maturity, and degradation (Ho and others, 1974, Bolshakov, 1986). Thiophenes were among the first OSC reported in oil and coal tar (Meyer 1882; referenced by Constantinides and Arich, 1967). Since that time, a large number of OSC have been identified in crude oil (Ho and others, 1974; Hughes, 1984; Bolshakov, 1986; Payzant and others, 1985, 1986; Sinnighe Damasté and others, 1987c). Developments in research into OSC in crude oils prior to 1967 were reviewed by Constantinides and Arich (1967). Much less is known about the distribution of OSC in sediments and source rocks, although much research recently has been focused on this subject (Hughes, 1984; Valisolalao and others, 1984; Brassell, 1986; Sinnighe Damasté and others, 1987a, 1987b, 1987c, 1988a, 1988b, 1989a, 1989b; Sinnighe Damasté and de Leeuw, 1987; Vairavamurthy and Mopper, 1987; ten Haven and others, 1988).

Recently, analytical methods have been developed which allow more detailed characterization of OSC in both crude oils and rock or sediment extracts. In addition, sulfur compounds have been obtained from high-molecular-weight fractions of crude oil and from kerogens by pyrolysis (Giraud and Bestougeff, 1967; Sinnighe Damasté and others, 1988a) and by selective chemical degradation of kerogen or other high-molecular-weight material (asphaltenes) (Sinnghe Damasté and others, 1988b). These analytical developments have led to a better understanding of the timing and mechanism of sulfur incorporation in sedimentary organic matter and have resulted in a rapid growth of research activity in this area.

Of considerable importance is the timing and mechanism of sulfur incorporation in sedimentary organic materials, because the practical application of organosulfur chemistry in petroleum geochemistry depends on understanding the relationship between the distribution of OSC and source rock deposition and secondary effects in oils (maturation, migration, degradation). Early work

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ers concluded that OSC found in crude oil could not have been present in the organic matter initially deposited in source rocks because sulfur compounds in living systems are not present in the amounts and molecular distributions found in sedimentary organic matter and crude oils (Birch, 1953; Constantinides and Arich, 1967). Further, the present consensus view is that sulfur is not added in significant amounts after oil has been generated (Gransch and Posthuma, 1974; Orr, 1978). It seems likely that most of the OSC found in crude oils are derived from kerogen in the source rock and are formed during early diagenesis of the organic matter. Constantinides and Arich (1967) suggested that elemental sulfur or H_2S could react with di-unsaturated hydrocarbons during early diagenesis to yield the thiophene series of OSC. Subsequent investigations by Sinnighe Damasté and coworkers (1987a,b, 1988b, 1989a) have provided substantial support for this hypothesis.

Gransch and Posthuma (1974) presented a conceptual framework for incorporation of sulfur into sedimentary organic matter in which high- and low-sulfur kerogens (and associated crude oils) are a function of the chemistry of the depositional environment of the source rock. Their scheme depended on the oxidation-reduction potential of the sediment (the presence or absence of sulfide) and whether or not reactive iron is present, which would effectively remove sulfide from the system before it could react in less kinetically favored organic reactions. Therefore, in depositional settings where reducing conditions coexist with small amounts of iron, sulfide could be present in sufficient quantities to react with organic matter to form high-sulfur kerogens. This reasoning is commonly used to explain high sulfur contents observed in many crude oils known to be derived from carbonate source rocks, and is sometimes used in the reverse manner as evidence that a particular oil may have been derived from a carbonate source rock. In contrast, depositional settings where greater quantities of reactive iron are present usually produce low-sulfur kerogens because most of the sulfur precipitates as iron sulfides before reactions with the organic matter can occur. This situation is typical for deposition of shale source rocks, although if enough sulfide is present or reactive iron content is relatively small, kerogens contained in shales may also have high sulfur contents. In general, oils derived from carbonate source rocks contain higher sulfur contents than oils derived from shale source rocks (Palacas, 1988).

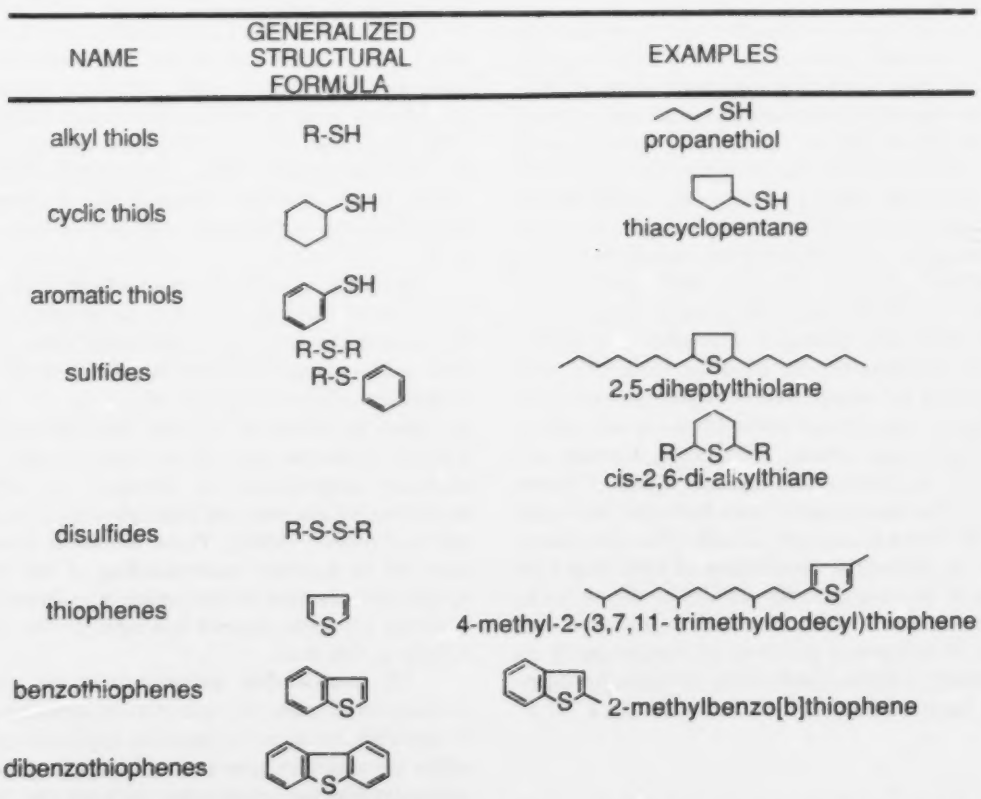

Figure 4. Classes of sulfur compounds reported in rock extracts and crude oils (after Ho and others, 1974; Sinnighe Damasté and others, 1987c). S, sulfur; H, hydrogen; R, alkyl group.

Research in the area of sulfur geochemistry of sediments and oils is likely to remain quite active for the next several years. Besides applications in oil-source rock correlations, maturity studies, and kinetic models of oil generation, sulfur geochemistry may play an important role in interpretations of the diagenetic and thermal history of hydrocarbon compounds as well. For example, hydrocarbons that would otherwise be present in a rock extract can be incorporated into the resin, asphaltene, or kerogen fraction by sulfur bonding. Thermal desulfurization can later release these "trapped" hydrocarbons. The importance of this process is that research and applications using hydrocarbons contained in rock extracts must take into account the sulfur pathway as a sink or a source of hydrocarbons during the thermal evolution of organic matter and generation in petroleum.

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The Geochemistry of Evaporites and Associated Petroleum

By Donald E. Anders *and* Robert J. Hite[1]

INTRODUCTION

Nearly two-thirds of the world's known petroleum resources are associated with evaporites (Nehring, 1978; Perrodon, 1978). The most noted of these are the giant oil fields of the Middle East (500 billion bbl), which are believed derived from the Arabian Gulf evaporite facies and the Arabian-Persian carbonate platform. In spite of the fact that enormous amounts of oil are associated with evaporites, the exact nature of this relation remains unclear. Some researchers have sought to unravel this mystery by studying the relation between biomass production and evaporitic environment (Copeland and Jones, 1965; Kirkland and Evans, 1981; Warren, 1986; Hite and Anders, in press); others have sought to explain the spatiotemporal relation between evaporitic volumes and oil volumes (Szatmari, 1980; Kalinko, 1974; Hite and Anders, in press); while still others have chosen to address the geochemical relation between oil and associated evaporites (Palacas, 1984, 1988; Hite and Anders, in press). A comparison of oil volumes (Parparova and others, 1981) to evaporite volumes (Zharkov, 1981) by Hite and Anders (in press) shows a strong spatiotemporal relation between oil and evaporites of the Upper Devonian, Lower Cretaceous, and lower Neogene but no relationship with major evaporitic occurrences in the Lower Cambrian and Lower Permian. In basins showing a strong relation between petroleum and evaporite volumes, 46 percent of the oil and gas reservoirs occur below the evaporites, 41 percent above the evaporites, and 13 percent within the evaporite facies (Kalinko, 1974). Hite and Anders (in press) offered several possible explanations for why large volumes of evaporites do not always have large volumes of associated hydrocarbons: (1) not all evaporite depositional environments are conducive to the accumulation of organic matter sufficient to generate commercial quantities of hydrocarbons (such as the shallow-water oxic environments of the midcontinent evaporites); (2) appropriate reservoirs and traps for evaporitic petroleum never developed or developed after migration; and (3) most occurrences of petroleum associated with evaporites are genetically related to evaporitic carbonate sediments which are not included in evaporite volume data. Whatever the reasons for this disparity, it is well documented that evaporitic environments can produce abundant biomass while providing excellent conditions for preservation of organic matter (Copeland and Jones, 1965; Neev and Emery, 1967; Nissenbaum and others, 1972, Cohen and others, 1977; Degens and others, 1978; Imhoff and others, 1979; Sackett and others, 1979; Sturm, 1980; Hammer, 1981; Kirkland and Evans, 1981; Northan and others, 1981; Lyons and others, 1982; Boon and others, 1983; Hite and others, 1984; Spencer and others, 1984; Klug and others, 1985; Schidlowski and others, 1985; Warren, 1986; and many more).

Evaporite environments and the rock types derived from them (carbonate, sulfate, and chloride minerals) cover a wide range of salinities from 35 permil (vitasaline) to over 350 permil (supersaline)(Lang, 1937; Kirkland and Evans, 1981; Hite and Anders, in press). Biomass production at various salinity stages in modern evaporitic environments generally increases with increasing salinity while the number of life-forms decreases with increasing salinity (Copeland and Jones, 1965; Klug and others, 1985). Green algae and cyanobacteria dominate the biomass of lower salinities while halophilic bacteria dominate the higher salinities (Javor, 1983; Sammy, 1985). Preservation of organic matter is greatest in the anoxic environments of the higher salinities where burrowing and grazing organisms and aerobic bacteria find it difficult to survive (Friedman and others, 1973; Gerdes and Krumbein, 1984). However, high productivity and preservation do not necessarily mean high organic matter content in evaporitic rocks of higher salinities. This seeming contradiction is the result of high precipitation rates for evaporite minerals, which dilute the solid organic matter in the sediment (Hite and Anders, in press). Also, dissolved organic matter may be excluded from precipitation and never become a factor in organic matter content of evaporitic rocks unless the evaporitic environment is totally desiccated (Hite and Anders, in press).

By far the most important evaporitic source rocks with respect to petroleum generation are carbonates. Carbonate source rocks often contain dark organic-rich laminated carbonate (marls) and argillaceous zones that can act as principal source material for petroleum generation (Hunt, 1968; Palacas and others, 1984). Carbonates can be excellent reservoirs as well (von Englehardt, 1977). Associated evaporites (anhydrite, halite, and potash) are often the cap rocks for such reservoirs. Although

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organic matter productivity in brines producing only carbonates is generally much lower than in higher salinity environments, carbonate deposition rate is the slowest of all minerals in the evaporite depositional cycle, thus allowing total organic matter values to rise above values found in more rapidly precipitating mineral stages. Carbonate-halite precipitation rates can be as low as 1:400 (Hite and Anders, in press).

GEOCHEMISTRY OF EVAPORITE ROCKS

Marine Carbonates

The organic chemistry of marine carbonate rocks is much better known than for other evaporite minerals (Palacas, 1984; Palacas and others, 1984). For a review of pertinent literature pertaining to carbonate source rocks of petroleum, see Palacas (1988). Organic carbon content of carbonate rocks is highly variable, with values as high as 10 to 30 percent being reported (Spiro and others, 1983; Palacas, 1984; Palacas and others, 1984; Powell, 1984). However, most carbonate source rocks have total organic carbon values in the range 0.5 to 5.0 percent (Palacas, 1984; Palacas and others, 1984; Sassen and others, 1987; Clark and Philp, in press). Bitumen extracts from marine evaporitic carbonates generally show pristane/phytane ratios below 1, however, values can be above 1 depending on the type of organic matter input and the reducing potential of the sedimentary environment (Didyk and others, 1978). Phytane/n-C_{18} ratios are generally above 0.5 and often above 1. The carbon preference index (CPI) is usually equal to or less than 1 (nC_{22}–nC_{32}) but can show odd-carbon predominance (CPI > 1) where there has been terrestrial organic matter input into the sediments. Nonhydrocarbon/hydrocarbon ratios are variable, depending on maturity, but generally exceed 0.35 in immature to moderately mature carbonate rocks. The C_{24} tetracyclic abundance is usually larger than the C_{26} tricyclic terpane pair. Hopanoid concentrations generally exceed sterane concentrations, and the C_{27}/C_{29} sterane ratio is between 1 and 1.5. Methyl isomers of dibenzothiophene generally form a V-pattern in relative distribution in moderately mature samples but a stairstep distribution in mature samples (Hughes, 1984). Sulfur contents (organic and elemental) are generally higher in carbonate extracts than in shale extracts. The C_{23} tricyclic terpane peak is commonly the dominant tricyclic terpane. For further geochemical characteristics of organic matter in carbonates, see Palacas and others (1984, 1988), Mello and others (1988), and Hite and Anders (in press).

Lacustrine Carbonates

The hydrocarbon chemistry of bitumen extracts from carbonate-rich lacustrine rocks does not resemble that of marine carbonates in all aspects, largely due to a greater influx of terrestrial oxidized organic matter into lacustrine sediments. This terrestrial component is commonly sufficient to influence CPI values and give strong odd-carbon predominance in n-alkane distributions and to change C_{27} and C_{28} sterane dominance to C_{29} dominance. Other differences are seen in the dominant tricyclic terpane (frequently C_{20} or C_{21} instead of C_{23}) and in relative abundance of hopanes/steranes is greater than 1 (< 1 in thermally immature rocks). Perhaps the two most distinguishing biomarker characteristics of open-lacustrine carbonate extracts are the great dominance of nC_{17} over other n-alkanes and the abundance of carotane isomers (β-carotane dominating). β-carotane is only minimally present in marine carbonates but is very abundant in lacustrine carbonate (Murphy and others, 1967; Anders and Robinson, 1971; Clark and Philp, in press). For further geochemical properties of lacustrine carbonates, see Hite and Anders (in press).

Anhydrites

Anhydrites are dense impermeable rocks whose organic matter genetically resembles the algal-rich type I and II kerogen, however, their organic content is usually too low for them to be considered viable source rocks (< 0.3 percent total organic content). One noted exception is the high organic carbon values (up to 30 percent total organic content) reported by Richardson and others (1988) for intrahalite beds consisting of laminated clays, magnesite, and anhydrite from the north Red Sea/Gulf of Suez Syn-Rift evaporite sequence. The authors theorized that these organic-rich zones are a result of algal blooms occurring during episodic freshening events. The importance of these thin organic-rich evaporite deposits as hydrocarbon source rocks remains to be seen.

Organic geochemical data on anhydrites are limited (Connan, 1981; Palmer and Zumberge, 1981; Gardner and Bray, 1984; Connan and others, 1986; Hite and Anders, in press). Because of the highly reducing environment of anhydrite deposition, pristane/phytane ratios are less than 1, phytane/n-C_{18} ratios are somewhat variable but generally greater than 1, CPI is less than 1 (nC_{22} to nC_{32}); in relative concentrations, pentacyclics > steranes > tricyclics, C_{24} tetracyclic > C_{26} tricyclics, C_{29} steranes > C_{27} or C_{28} steranes; and extended hopanes (C_{31}-C_{35}) are abundant.

Halite and Potash

Volumetrically, halite and potash are the most abundant of the evaporite minerals. One author, Szatmari (1980), suggests that via dissolution mechanisms halites could be the principal source rocks of the world's largest oil deposits. In spite of the volumetric favorability

of halite and potash as source rocks and the organic richness of halite- and potash-producing brines (300 + permil salinity range), the organic carbon contents of halite and potash seldom exceed 0.3 percent, and the majority has less than 0.01 percent TOC. The general consensus is that TOC values this low are insufficient to be considered a source rock (Hite and Anders, in press). Consequently, few studies of the organic geochemistry of halite and potash rocks have been reported. One report by Hite and Anders (in press), of Paradox and Permian Basin halites, gave the following general characteristics: pristane/phytane ratios 0.9 to 1.1, CPI generally less than 1 (nC_{22} to nC_{32}), relative concentration of hopanes exceeds steranes, C_{23} tricyclic terpane is the dominate tricyclic terpane, C_{24} tetracyclic > C_{26} tricyclics, and the nonhydrocarbon/hydrocarbon ratio (non-HC/HC) is usually less than 0.3.

GEOCHEMISTRY OF EVAPORITE SOURCED OILS

Most of the geochemical information on oils derived from evaporite rocks is for oils associated with marine and lacustrine carbonates. For marine carbonate oils, see the literature survey by Palacas (1988) and Mello and others (1988). For lacustrine carbonate oils, see Tissot and others (1978), Mason (1981), Poole and Claypool (1984), Fleet and others (1988), and Mello and others (1988). Geochemical data on oil derived from anhydrite, halite, and potash are much more limited (see Hite and Anders, in press).

Marine Carbonate Oils

Marine carbonate oils have the following general geochemical characteristics: full range of API values from less than 20° to more than 50°, sulfur content usually greater than 1 percent, pristane/phytane less than 1, CPI less than 1, non-HC/HC is 0.1 to 0.5, relative abundance of hopanes exceeds steranes, C_{27} steranes/C_{29} steranes variable, moderate amounts of tricyclic terpanes (C_{23} maxima), abundant extended hopanes (C_{31}–C_{35}), C_{24} tetracyclic terpane > C_{26} tricyclic terpanes, and V-shaped distribution for methyldibenzothiophenes (Hughes, 1984). Additional organic geochemical properties are discussed by Palacas (1988) and Hite and Anders (in press).

Lacustrine Carbonate Oils

Lacustrine carbonate oils can have variable geochemical features depending on whether they are derived from organic matter dominated by type I kerogen (such as some of the Uinta basin oils) or some combination of types I and III kerogens (such as found in China basins). Generally, API values range from 20° to over 40°; sulfur contents less than 1 percent in oils from iron-rich sediments, pristane/phytane and CPI values are both less than 1 in oils derived from sediments deposited under anoxic, reducing, open-lacustrine evaporitic conditions but frequently greater than 1 in oils derived from both lacustrine biota and oxidized organic matter from continental sources; non-HC/HC is 0.2 to 1.7; relative abundance of steranes > hopanes > tricyclics in moderately mature oils, but hopanes > tricyclics > steranes in mature oils; C_{27} steranes < C_{29} steranes where continental input is a factor; tricyclic terpane maxima usually C_{20} or C_{21} but rarely C_{23}; minimal extended hopanes; moderate gammacerane and abundant carotenoids.

Anhydrite Oil

Geochemical data for oils derived from anhydrite rock are limited (Hite and Anders, in press). Based on the work of Hite and Anders (in press), the following geochemical properties were observed: pristane/phytane less than 1; phytane/n-C_{18} greater than 1; non-HC/HC up to 30 percent; hopanes > steranes; moderate to abundant pregnane; C_{27} steranes < C_{29} steranes, minimal to moderate tricyclic terpanes (maxima C_{23}); C_{24} tetracyclic terpane (abundant) > C_{26} tricyclic terpanes; and abundant extended hopanes (maxima C_{35}). Palacas and others (1984) mentioned a number of oil shows in the Punta Gorda Anhydrite (south Florida) but stated that these shows were generally associated with carbonate-rich facies in the anhydrite zone. The authors did not know whether these oil stains were carbonate or anhydrite derived. Likewise, Clark and Philp (in press) reported on the possible evaporite origin of some oils of the Black Creek Basin, Ontario. Like the Punta Gorda source rocks, the Black Creek oil source rocks were interbedded carbonates and anhydrites.

Halite and Potash Oil

The geochemical characteristics of halite-potash oils are based primarily on data from seeps in potash mines in the Paradox (Utah) and Permian (New Mexico) basins and a seep in a halite mine (Pugwash) in New Brunswick. Additional data were obtained from oil inclusions and stained halite core from the Paradox basin (Utah)(see Hite and Anders, in press). Sulfur content in the halite-potash oils is generally less than 0.1 percent. Sulfur isotopic values approach –19 permil and carbon isotopes –30 permil. Pristane/phytane ratios were 1 or greater. If low pristane/phytane ratios (< 1) reflect depositional environment, as some have suggested (Brooks and others, 1969, Didyk and others, 1978, ten Haven and others, 1987, and others), the observed values reported by Hite and others (1984) and Hite and Anders (in press) are a bit high. On the other hand, if these pristane/phy-

tane values reflect not only the values of the depositional environment but possible input from organic matter sources outside the basin, the values could be expected to be higher. Hite and others (1984) offered corroborating data in support of transport of oxidized organic matter into the Paradox basin. Other geochemical properties of halite-potash oils are: CPI greater than 1 (C_{15}–C_{17}), but no preference for the remaining *n*-alkanes, non-HC/HC is less than 30 percent, abundance of hopanes > steranes, C_{27} steranes > C_{29} steranes, abundant diasteranes, moderate amounts of tricyclic terpanes (maxima C_{23}), C_{24} tetracyclic > C_{26} tricyclics, and moderate amounts of extended hopanes (maxima C_{31}).

SUMMARY

Evaporite depositional environments can be excellent settings for the production and preservation of hydrogen-rich organic matter. Evaporite rocks, though generally lower in organic carbon content than shales, have two to eight times as much extractable organic matter per gram of organic carbon as do shales (Tissot and Welte, 1984, p. 97). Under the proper conditions of time and temperature, much of the organic matter associated with evaporites is converted to hydrocarbons. Because of their low permeabilities, evaporite rocks make effective seals against fluid and gas migration, thus much of the generated hydrocarbon is kept locked in the evaporite sequence. However, through dissolution, bacterial reworking, and diapirism evaporates can become good reservoirs as well. We have only begun to understand the value of evaporites in relation to petroleum generation. Future work will undoubtedly challenge our present ideas and concepts.

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Effect of Biodegradation on Crude Oils

By G. Eric Michael[1]

The use of molecular parameters and bulk properties of oil or rock extract is common practice for making oil-to-oil, oil-to-source rock correlations and maturity determinations in petroleum exploration. However, biodegradation of oils from reservoir rocks or surface seeps can add to the difficulty of establishing a correlation or a level of maturity based on bulk or molecular properties. The link between biodegradation and the conditions under which biodegradation occur are important to know when interpreting hydrocarbon history. Bulk oil properties, such as API gravity, sulfur content, $\delta^{13}C$, $\delta^{34}S$, and percent saturates and aromatics, are altered with only low to moderate degradation (Seifert and others, 1984; Connan, 1984). Increased optical activity and destruction or alteration of sterane and terpane biomarkers result from more extensive biodegradation (Seifert and Moldowan, 1979).

The status of research into crude oil biodegradation is here organized relative to increasing alteration. It should be stressed that severity of biodegradation is not absolute and exceptions are common. The exceptions to the general trend in degradation is the result of many different variables such as pH, Eh, time, temperature, and microbial species. In general, the smaller and simpler the structure of an organic molecule, the more likely it is to be biodegraded.

A synopsis is also given toward biomarkers or petroleum fractions that might be of particular use in very extensively biodegraded oils. Porphyrins, tricyclic terpanes, mono-aromatic and triaromatic steroids, and pyrolysis-gas chromatography (py-GC) of asphaltene fractions appear to be good correlation tools for extensively biodegraded oils.

Table 4 summarizes biodegradation parameters commonly used in oil exploration. The effects due to biodegradation on $\delta^{13}C$ and $\delta^{34}S$ isotopes of whole oil and oil fractions are not addressed here (see Stahl, 1980, and Hartman and Hammond, 1981).

The saturated hydrocarbon fraction of oil is usually the first affected by only light biodegradation. However, exceptions to the relative order of biodegradation are still being discovered as research progresses. The typical order is preferential removal of light *n*-alkanes followed by removal of iso- and anteiso-alkanes and then isoprenoids (Alexander and others, 1983; Connan, 1984). Upon moderate to extensive degradation, polycyclic molecules are then attacked within the saturate hydrocarbon fraction.

The steranes and diasteranes are preferentially removed in the order of $C_{27} > C_{28} > C_{29}$ (Goodwin and others, 1983). Biodegradation of steranes shows stereoselective removal of the biological 5α,14α,17α 20R isomer (Rullkötter and Wendisch, 1982; McKirdy and others, 1983). The geological isomer 5α,14α,17α 20S is preferentially degraded over the 14β,17β series (Seifert and others, 1984, Chosson and Connan, 1989). Diasteranes are typically attacked after the C_{27}–C_{29} regular steranes with the 20S isomer attacked preferentially over the 20R isomer (Seifert and Moldowan, 1979). An exception to this order was found by Williams and others (1986) in south Texas crude oils, in which the steranes were not degraded but diasterane concentrations were significantly lowered. The regular steranes C_{21} and C_{20} appear to survive even after extensive biodegradation of steranes and diasteranes (Connan, 1984).

Volkman and others (1983) showed that hopane biodegradation immediately followed initial alteration of 5α,14α,17α 20R steranes. In an earlier study, Seifert and Moldowan (1979) observed hopane demethylation to be concurrent with sterane degradation. Goodwin and others (1983) showed the susceptibility of hopanes to biodegradation follow the order $C_{35} > C_{34} > C_{33} > C_{32} > C_{31} > C_{30} > C_{29}$. However, in a recent study of biodegraded tar-sand extracts, Lin and others (1989) showed biodegradation in the order $C_{30} > C_{31}$–$C_{33} > C_{34}$–C_{35}. The preferential removal of the biological 22R isomer hopane was confirmed in both studies. A number of studies have shown that extensive biodegradation of 17α(H)-hopanes produces a series of ring A/B demethylated hopanes (25-norhopanes) (Seifert and Moldowan, 1979; Rullkötter and Wendisch, 1982; Volkman and others, 1983). However, biodegradation of hopanes does not always produce ring A/B demethylated hopanes (Goodwin and others, 1983; Connan, 1984; Lin and others, 1989). Moreover, demethylated hopanes have been found in apparently nonbiodegraded oils (Philp, 1983; Volkman and others, 1983; Howell and others, 1984). The possibility that demethylated hopanes could originate from source rock has not yet been proved or disproved. Cassani and Gallango (1988) suggested that the presence of demethylated hopanes is related to the main site of biodegradation, surface or near surface

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Table 4. Commonly used geochemical parameters and how they are affected by biodegradation

[*, not affected or highly resistant; (?), questionable as to how the parameter is affected or at what level; HC, hydrocarbons; E, etio porphyrin; D, DPEP porphyrin; PH, phenanthrene; MPH, methylphenanthrene; DMPH, dimethylphenanthrene]

Parameter	Effect	Severity
Bulk properties, often continuous change with progressive effects		
API gravity	Decreases	Low–very high
Optical activity	Increases	Moderate–very high
Saturated HC/aromatic HC	Decreases	Low–moderate
HC/resins+asphaltenes	Decreases	Low–high
Total sulfur	Increases	Moderate–very high
Alkanes, followed by iso-,anteiso-alkanes, and isoprenoids		
Pristane/n-C_{17}	Increases	Low
Phytane/n-C_{18}	Increases	Low
Pristane/phytane	Decreases(?)	Moderate
Steranes, biodegraded after n-alkanes and isoprenoids		
Steranes/diasteranes	Decreases	High
Steranes/hopanes	Increases(?)	High–very high
5α(20S)/5α(20R)	Increases	High
C_{21}+C_{22}/C_{27}-C_{29}	Increases	High–very high
ααα-C27/ααα-C_{29}	Decreases	High
ααα-C_{28}/ααα-C_{29}	Decreases	High
Diasteranes, more resistant than C_{27}-C_{29} regular steranes		
C_{27}/C_{29}	Decreases	High–very high
20S-C_{27}/20R-C_{27}	Decreases	High–very high
Terpanes, C_{30}-C_{35} hopanes degraded while regular steranes degraded		
22S/22R hopanes	Increases	High
C_{27}-C_{29}/C_{30}-C_{35} hopanes	Increases	High–very high
Tm/Ts; norhopanes	*(?)	High–very high
Tri+tetra/pentacyclic	Increases	High–very high
Aromatics, some may be degraded prior to alkanes		
PH/MPH	Decreases	Moderate–high(?)
MPH/DMPH	Decreases	Moderate–high(?)
Mono-/tri-aromatic steroid	*	Very high
Porphyrins, appear not affected by severe biodegradation		
DPEP/ETIO	*	Very high
C_{28}E/(C_{28}E+C_{32}D)	*	Very high
Asphaltenes-resins, appear not affected by severe biodegradation		
Py-GC	*	Very high

versus subsurface, with demethylated hopanes being absent in surface or near-surface degraded samples. Moretanes, which appear more resistant than hopanes, show increased susceptibility to biodegradation with increased carbon number. The C_{29}-hopane, 17α(H)-22,29,30-trisnorhopane (Tm), and 18α(H)-22,29,30-trisnorneohopane (Ts) are particularly resistant to biodegradation (Seifert and others, 1984; Lin and others, 1989). Brooks and others (1988) found that the Ts/Tm ratio was not affected among biodegraded oil sands of western Canada. Tricyclic and tetracyclic terpanes appear to be highly resistant to biodegradation, as confirmed by Connan and others (1980), Goodwin and others (1983), and Lin and others (1989). However, tricyclic terpanes have been found to be demethylated similar to hopanes in severely biodegraded oils of the St. Aubin Asphalt, Switzerland (Connan, 1984).

The biodegradation of aromatic hydrocarbons is not as well understood as that of the saturated hydrocarbons. The general susceptibility of most aromatic compounds during aerobic degradation is monoaromatic > diaromatic > triaromatic (Connan, 1984). The best known exception to this order is the resistivity of monoaromatic and triaromatic steroids, which are resistant to biodegradation even after the C_{27}–C_{29} steranes, hopanes, and C_{27}–C_{29} diasteranes have been severely biodegraded (Volkman, 1984; Wardroper and others, 1985). It should be noted that Jones and others (1983) found that low-molecular-weight aromatic compounds apparently are not biodegraded under anaerobic conditions, but only under aerobic conditions.

Aromatic compounds that are alkyl-substituted have been shown to be biodegraded by a cooxidation pathway similar to that of *n*-alkanes (Raymond and others, 1971). In general, resistivity increases for the alkylaromatics as the number and length of alkyl substituents increase. Increased numbers of substituents, especially if adjacent, apparently cause steric hindrance effects which increase the resistance to microbes that use alkyl cooxidation. It should be mentioned, however, that oxidation of the unsubstituted ring can still take place aerobically, either by other microbes or under different environmental conditions. Different isomers of alkyl-substituted aromatics have been shown to be biodegraded at different rates (Rowland and others, 1986). An example of the previously mentioned factors in biodegradation of alkylaromatic compounds has been worked out for alkylnaphthalenes by Volkman, 1984. The order of susceptibility follows: naphthalene > 2–MN > 1–MN > 2,7–, 1,7– and 1,6–DMN > 1,3– and 2,6–DMN > 1,4– and 1,5–DMN > 1,2–DMN > 2,3–DMN and 1–EN > 2–E > 1,8–DMN (where MN is methylnaphthalene, DMN is dimethylnaphthalene, and EN is ethylnaphthalene). In some oil samples studied, the order of degradation of some alkylnapthalene isomers has been found to be switched and has been attributed to different environmental conditions (Volkman, 1984). Trimethylnaphthalenes are more resistant to biodegradation than naphthalene, MN, and DMN (Rowland and others, 1986). Biphenyl and 3-methylbiphenyl appear to both be at least as susceptible to biodegradation as the methylnaphthalenes (Rowland and others, 1986). Phenanthrene and methylphenanthrenes are more resistant to biodeg-

radation than naphthalene and methylnaphthalene (Volkman, 1984; Rowland and others, 1986). Phenanthrene appears to be more easily biodegraded than the methylphenanthrenes, of which the 9-isomer appears most resistant (Rowland and others, 1986). Sulfur content is known to increase with biodegradation, but it is unclear as to when these compounds are altered relative to other aromatic compounds. Degradation of sulfur-bearing aromatics has been reported in the literature (Connan, 1984), and benzothiophene appears to be degraded prior to dibenzothiophene (Connan, 1984).

Connan (1984) has shown that extensive alteration of both aromatics and alkanes is generally found only at the surface or at shallow depth, while in deeper reservoirs, highly altered aromatics and organosulfur compounds are associated with only mildly altered alkanes. Preferential alteration of aromatics over alkanes has also been observed in the laboratory (Rowland and others, 1986). In either case, the magnitude of unresolvable complex mixture in the GC-chromatograms for both the saturate and aromatic hydrocarbon fractions increases with increased biodegradation (Volkman and others, 1983; Brooks and others, 1988).

Considerable debate still exists among researchers as to whether the asphaltene and resin fractions are affected by biodegradation (Connan, 1984 and references therein). Teschner and Wehner (1985) demonstrated in laboratory experiments that py-GC products of asphaltenes are not affected by biodegradation. The resistance of asphaltenes to biodegradation has been further demonstrated in field studies by Rubinstein and others (1979), and Bonnamay and others (1987), who compared asphaltene pyrograms of biodegraded and nonbiodegraded oils.

Porphyrins, which appear to be highly resistant to biodegradation, are a class of biomarkers present in the more polar aromatic and resin fractions of rock extracts and crude oils. Barwise and Park (1983) found no change in porphyrin distributions for a suite of oils derived from a common source and of similar maturities but at different reservoir depths and subjected to different levels of biodegradation. Palmer (1983) demonstrated that DPEP/ETIO ratios of porphyrins are good maturity parameters when biodegradation has already affected parameters such as API gravity, *n*-alkanes, and sterane and hopane distributions. Michael and others (1989), in a study of tar sand extracts from core, found no evidence for alkyl side chain cooxidation of porphyrins, cleavage of the isocyclic ring in DPEP porphyrins, or other alteration of the tetrapyrrole ring structure, despite extensive biodegradation of steranes and hopanes.

Observed discrepancies in the order of biodegradation of compounds attests to the complication of studying a process which is undoubtedly subject to several variables. Further laboratory and field observations are required to understand how such variables as temperature, pH, Eh, growth factors, nutrient supply, and microbe species influence order and rate of biodegradation. In the future, with continued research, it could become possible to distinguish between primarily aerobic or anaerobic biodegradation processes. The ability to distinguish aerobic versus anaerobic degradation could be very useful in confirming current or paleohydrodynamic conditions of an oil reservoir.

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Heavy Oil and Natural Bitumen

By Richard F. Meyer[1]

INTRODUCTION

Original reserves of heavy oil in the United States are estimated to be 30.2 billion barrels and undiscovered resources are 4.3 billion barrels. In-place bitumen in the United States is estimated to be 22.9 billion barrels of demonstrated resources and 33.7 billion barrels of inferred resources (Meyer and Duford, 1989). An increasing need for new oil supplies indicates that increased research and exploration are necessary to make the heavy oil and bitumen fill at least a portion of this need.

Research directed toward heavy oil and natural bitumen in the United States is at a low level, except as reported in the U.S. Department of Energy symposia on Enhanced Oil Recovery and a few joint projects of the Department with industry. Most heavy oil in the United States has been and is produced in California. In 1988, 466,000 barrels of heavy oil per day (bbl/d) were produced in the United States by enhanced oil recovery methods: 97.8 percent by steam injection, 1.4 percent by in situ combustion, and small amounts by using chemical additives (Meyer and Duford, 1989). For 1979, Marchant and others (1981) reported five natural bitumen recovery projects: two by steam, two by combustion, and one utilizing mining. For 1985, Marchant (1988) reported 34 in situ and nine mining projects. Today there are no active recovery projects. Fortunately, two other Western Hemisphere nations, Venezuela for heavy oil and Canada for bitumen, have already made major strides in solving some of the research problems associated with the exploitation of these commodities.

DEFINITIONS

Definitions of heavy crude and bitumen are based upon either their physical or chemical properties or on a combination of the two. Although chemical analysis is rigorous, it is time consuming and the chemical composition is often reflected in the more easily measured physical attributes. The most readily available of these physical characteristics are the API gravity and the viscosity, and either or both of these are commonly used to set the limits of heavy crude and natural bitumen. The API gravity is expressed on a scale in which 10° is equivalent to a specific gravity of 1 and a density of 0.934 g/cm^3. Viscosity, the resistance to flow, may be expressed in poises (pascal-seconds), the quotient of shearing stress and velocity gradient. Heavy oil (Martinez, 1984; Byramjee, 1983) is defined as that oil having API gravity of 20° and extra heavy oil as that below 10°, regardless of viscosity. Natural bitumen is any oil having a viscosity greater than 10,000 centipoises (cP). Briggs and others (1988) include bitumen with heavy oil which is then defined as any oil more viscous than 100 cP. Refiners define heavy oil as any oil which will yield 15 percent residuum at a temperature of 1,010 °F (National Petroleum Council, 1980; Meyer, 1987). Another type of classification (Hunt, 1979) is based on the fact that bitumens are soluble in carbon disulfide, whereas pyrobitumens are neither soluble nor fusible. Among the bitumens, the application of heat discriminates natural asphalt, which fuses, from the asphaltites—such as gilsonite—which are difficult to fuse, and the mineral waxes—such as ozocerite—which are easily fused. Natural asphalt is by far the most important quantitatively and is a potential source of synthetic oil. Unless specifically stated otherwise, the term "natural bitumen" refers to, and is synonymous with, "natural asphalt." Connan and van der Weide (1978) point out the weakness of classifications based on physical attributes; these physical characteristics may result from immaturity of thermal evolution or postexpulsion alteration as well as from uninterrupted maturation. Nonetheless, a classification based upon physical characteristics (Martinez, 1984) is useful for the compilation of statistical data. The compiler must recognize that such a classification neither necessarily indicates the origin of the oil nor distinguishes between immature oil and oil that which has been subjected to alteration. The origin bears upon the methods employed for resource assessment and on the recovery of the oil from known deposits.

RESOURCES

In the United States, about one-third of the original reserves of heavy oil, about 10 billion barrels, are in giant fields having recoverable original reserves of 500 million barrels each; 8 of the 10 giant fields are in California (Meyer and Duford, 1989). Heavy oil is identified in 44 U.S. petroleum provinces, of which 5 contain

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giant fields and 4 contain offshore fields. Bitumen deposits are found in 17 petroleum provinces. Although many of the deposits have served as sources of direct-use asphalt in the past, no natural bitumen is being produced in 1989. Of the 56.6 billion barrels of in-place bitumen in the United States (Meyer and Duford, 1989), two-thirds is contained in four provinces: the Uinta basin (23 percent), the Arctic Coastal Plain basin (19 percent), the Warrior basin (14 percent), and the Paradox basin (11 percent).

CHEMISTRY

Typically, the heavy oils and natural bitumens have high molecular weight and viscosity, low *n*-alkanes, high asphaltenes and resins, high sulfur, and high trace metals, especially nickel and vanadium. The composition of heavy oil and bitumen is a function of source rock type, thermal maturation, and alteration, three processes that operate singly or in combination. Generally, a carbonate source rock expells oil that contains more nitrogen-sulfur-oxygen (NSO) compounds than a siliciclastic source rock. Low maturity is indicated by few hydrocarbons, many NSO compounds, high molecular weight, high sulfur to nitrogen ratio (S/N), low API gravity, and high viscosity (Waples, 1985). Silverman (1978) stated succinctly that maturation leads to an increase in saturate-hydrocarbon and gasoline contents and a decrease in NSO compounds, whereas degradation has the opposite effect, *n*-alkanes are reduced and the asphaltene and NSO contents are greatly increased.

The alteration of an oil after it is expressed from a source bed can take many forms. Cracking, in which large molecules are reduced to smaller ones, is a part of the maturation process due to increase in temperature and pressure consequent to greater depth of burial and may eventually lead to thermogenic gas and ultimately to graphite. The effects of temperature on the maturation of organic matter and petroleum are well known (Hunt, 1979; Waples, 1985), and temperature has been correlated with many indices of maturation (Heroux and others, 1979). Pressure effects have been both acknowledged (Tissot and others, 1974) and denied (Hunt, 1979) as an important factor in petroleum generation. Both hydrostatic and lithostatic pressure increase with depth, as does temperature; pressure also is basic to the cracking of oil in refineries. Pressure therefore appears to play a significant role in petroleum generation and, in particular, to the evolution of heavy oil and bitumen and should be accorded research effort. Nonthermal alteration leads to degradation of the oil through the processes of deasphalting, water washing, and biodegradation. Deasphalting is the precipitation of the large, heavy asphaltene molecules by natural gas and gravity segregation, often forming a tar mat at the oil-water contact. Water washing is a process of selective dissolution of certain lighter components of the oil by water, but the effects are generally small (Waples, 1985) and will not lead to development of a tar mat (Lafargue and Barker, 1988). Biodegradation by bacteria in the oxygenated zone is the most important degradation process. It may commence during secondary migration through the carrier bed from the source bed to the reservoir but most commonly takes place after the entrapped oil is elevated into the zone of oxidation. The result is a surface or near-surface natural bitumen deposit. Waples (1985) and Connan (1984) have summarized the effects of biodegradation. In order of preference the bacteria attack: (1) the *n*-alkanes, (2) the long alkyl side-chains, (3) the single methyl branches or the widely spaced branches, (4) the isoprenoids, and (5) the polycyclic alkanes. No evidence indicates that bacteria affect porphyrins, asphaltenes, or the heavy NSO compounds. Thus, alkanes may be reduced from their normal 60 percent of the oil to 20 percent, with consequent increase in aromatics and polar compounds. Sulfur may be increased proportionately by hydrocarbon removal and by sulphate reduction.

The heavy oil and bitumen are highly viscous because of their high content of asphaltenes. In laboratory analysis with solvents, *n*-pentane precipitates the asphaltenes. Condensate, including pentane, is also used as a diluent to move heavy oil and bitumen through pipelines (Todd, 1988). Consequently, the volume of solvent mixed with the oil is critical to prevent precipitating asphaltenes that would clog pipelines and disrupt delivery of the oil to refineries. Research is being conducted on diluents to determine the correct amount to be used to avoid precipitation and on the positive effects of adding carbon dioxide (Fuhr and others, 1989) as well. Excessive asphaltenes tend to foul refinery crude exchangers (Dickakian and Seay, 1988) and other equipment. Research is required on the role of asphaltenes not only in condensate mixtures but also on refinery feed stocks when two or more asphaltic crudes are to be combined.

Asphaltene precipitation is manifested in another way by the formation of tar mats in numerous oil fields. Haldorsen and others (1988) describe the tar mat in the Prudhoe Bay field. Hirschberg (1988) discusses compositional variations in the fluid columns of reservoirs, citing the tar mat as the extreme example. The tar mat can seriously impede the flow of water in the reservoir, either naturally or when waterflood recovery is attempted. The presence of tar mats reduces or hampers oil recovery.

CATALYSIS

In refining crude oil, catalytic cracking is used in preference to thermal cracking because reaction rates are faster, lower temperatures are needed, less coke and

gas are produced, and more branched alkanes result, yielding a higher octane rating (Neumann and Rahimian, 1984). The aluminum silicate catalysts which made catalytic cracking economic consisted of naturally occurring bentonite, later succeeded by synthetic montmorillonite. In nature, according to Waples (1985), the role of catalysis is not proved but probably varies with the particular clay mineral. It is generally accepted that the result of petroleum maturation reflects the nature of the original organic matter that formed the kerogen of the source rock, the temperatures to which the source rock and, later, any expelled petroleum, were exposed, and the geologic time involved during which the genetic process takes place. Goldstein (1983) makes a compelling argument for the place of geocatalytic reactions in the generation of oil. He identifies two energetically difficult reactions required for oil formation: shortening of alkane chains by cracking to produce gases and light oils, and fatty acid decarboxylation to yield *n*-alkanes. Without catalysts, these reactions can only take place in the laboratory at temperatures above 752 °C. Such reactions do, in fact, occur naturally. Hunt (1979) reviews the subject of geocatalysis, concluding that activation energies for many reactions require something other than straight thermal cracking, including lower energies involved in simultaneous reactions. Other explanations may be possible for the differences between laboratory experiments and extrapolations into geologic time. Milner and others (1977) presented views for and against natural catalysis but suggested that geocatalytic cracking may be a factor. Freund and Keleman (1989), on the basis of studies of low-temperature pyrolysis, believe that the time required for natural oil generation can be explained by measured high-temperature kinetics, which are stated to be valid at temperatures as low as 209 °C. They feel that geocatalysis may be possible but is not necessary. However, 209 °C is still at or near the upper limit of the oil generation zone. Additional research is necessary to establish whether geocatalysis is effective in the oil-generation process.

OIL SEEPS

Oil seeps are common throughout the world. They provided a source of bitumen in antiquity for caulk and cement and were one of the earliest surface indicators to be used in oil exploration. Lists of some of the better-known seeps are given in Abraham (1960), Forrer (1986), and Meyer and Fleming (1986). Thompson (1934), Hunt (1979), and Forrer (1986) described the characteristics of oil seeps and their use for direct exploration and as guides to shallow buried deposits. Seeps may owe their origin to various causes: exhumed and degraded conventional oil deposits, exhumed immature deposits, or the surface manifestation of a liquid oil deposit whose carrier bed has been breached by erosion and is now exposed at the surface. Knowledge of the characteristics of individual seeps bears directly upon the proper interpretation of petroleum systems involving heavy oil and natural bitumen deposits.

UNDISCOVERED RESOURCES

There is no certain way to assess the quantity of the undiscovered resource of heavy oil, even more than light oil, in a given basin. The method used by Meyer and others (1984) was simply to determine the proportion of reserves in a basin that were heavy oils and apply that proportion to the total undiscovered oil, as determined by others (for example, Dolton and others, 1981). These assessments are inaccurate because conventional assessment methods do not include heavy oil, except in fields under production at the time of the estimate, or bitumen deposits (McKie, 1982), and the methods themselves have specific deficiencies. Procter and others (1982) devised a method of play analysis which they have applied to heavy oil in Canada. A review of heavy oil assessment methods by Meyer and Schenk (1986) stresses the need for considering material balances to account for the loss of as much as 80 percent of the original oil through various degradation processes. However, the estimation of possible amounts of undiscovered oil alone is not enough to be useful for planning. Some idea of the potential for recovery must also be applied. Innovative research on this subject is reported by Connan and Coustau (1987). Their studies emphasized the necessity for distinguishing immature oil (Petersen and Hickey, 1987; Clayton, 1989) from mature, but degraded, oil. If degradation preceded accumulation or if the oil is immature, the oil will contain large molecules and will be highly viscous. Thus, it can saturate only the most permeable and porous zones in the reservoir, making recovery by steam flooding efficient. But if the oil was originally light, it could have entered the less permeable and less porous zones in the reservoir. After degradation, these zones contain very viscous oil and are very difficult to sweep efficiently, which may lower the recovery to or below the economic limit, effectively reducing the recoverable oil assessment.

The assessment of natural bitumen resources is more straightforward than for heavy oil because the deposits are mostly at the surface or occur at shallow depths in proximity to surficial deposits. Historically, most such deposits have been located by surface geological exploration; however, means are now available to search for natural bitumens by remote sensing (Cloutis, 1989). Moore (1984) summarized the ways in which asphalt deposits (tar seals) can be utilized for exploration by indicating buried deposits either below the seals, along basin margins, or in stratigraphic traps.

The role of economics is extremely important in determining feasibility of recovery from bitumen deposits. The deposit grade and size are of fundamental importance (Meyer and Schenk, 1986; Earley, 1987).

ASSESSMENT BY PETROLEUM SYSTEM

The concept of petroleum systems (Magoon, 1988) offers the best opportunity for assessment of heavy oil and natural bitumen resources because the development of such systems is based on geological fact and intuition rather than on simple statistical data manipulation. Evaluation factors include the level of system certainty; source rock age, lithology, thickness and kerogen type; reservoir-rock age, lithology, and thickness; and overburden age, lithology, and thickness. Information on hydrocarbon maturity, degradation, chemical attributes, and richness may readily be added for heavy oil and bitumen. The ages can be established by use of the U.S. Geological Survey geologic names handbook (Swanson and others, 1981), and derived computer printout sheets can provide the appropriate geologic province name. The timespans for generation, accumulation, and degradation can be estimated from geologic time scales, such as contained in Harland and others (1982). These data, and information from available boreholes, will provide a data base for an accurate assessment of the potential volume of petroliferous sediment. Pusey (1973) and McDowell (1975) outlined the general principles of basin-potential evaluation.

Cooles and others (1986) gave formulas for calculating petroleum masses generated and expelled from source rocks. They concluded that rich source rocks having organic carbon in excess of 1.5 percent may lead to the expulsion of 60 to 90 percent of oil generated, whereas expulsion from leaner source rocks is correspondingly less efficient. Tannenbaum and others (1987) showed that in the conversion of light oil to heavy oil as much as 80 percent of the oil volume may be lost. Moshier and Waples (1985) demonstrated that, in addition to those present in the rock body, in which the Athabasca reservoir rocks are located, additional source rocks are required to supply the quantity of petroleum present in the Athabasca deposits. Similarly, Nalivkin and others (1984) calculated that 65 percent of the oil that originally migrated into the Olenek deposit in Siberia was lost by degradation. The amounts of oil lost by degradation in the world are staggering. Hunt (1979) estimated that the asphalt deposits of the world contain about 2 trillion barrels of oil, a very conservative estimate. He calculated that, had these deposits originally been of 35° API gravity oil, their volume would have been 9.5 trillion barrels. Use of the petroleum system approach will make possible the estimation of the age and span of time in years when such oil was lost.

OTHER POTENTIAL RESOURCES

Heavy oil and natural bitumen are rich in organometallic complexes as well as sulfur. In the United States in 1987, 58 percent of sulfur production was derived from petroleum operations, 30 percent from Frasch native sulfur plants, and only 12 percent as byproduct of metals plants. World vanadium production exclusive of the United States, where data are proprietary, was 34,000 short tons in 1987 from slags, concentrates, and ores. Production from petroleum refineries from residues, ashes, and spent catalysts amounted to 925 tons in Japan and 2,504 tons in the United States, mainly from refineries processing imported Venezuelan heavy crudes, which are very high in metals. Vanadium is also recovered from petroleum residues in the Federal Republic of Germany and other European countries, and USSR (U.S. Bureau of Mines, 1989). Gribkov (1989) has made the point that the nonhydrocarbons may make some bitumen deposits economic and may, in some deposits, be of greater value than the bitumen. In a current study, C.A. Palmer (written communcation), based on analyses of 27 samples from 10 natural bitumen and heavy oil deposits, reports identifying 38 trace metals plus sulfur. The sulfur is most common, with a maximum determination of 69,000 parts per million.. Metals with high determined values include iron, potassium, sodium, vanadium, strontium, nickel, barium, and zinc.

CONCLUSION

Research on heavy oil and bitumen may expand avenues of interest to many petroleum disciplines. The geochemist may gain increased knowledge of the evolution of petroleum hydrocarbons, particularly the role of natural catalysts. The geologist may improve methods for the assessment of resource levels and attain characterization of the oils and reservoir rocks to assist in enhanced recovery. The chemist may achieve detailed analysis of the hydrocarbon's chemical composition to aid in planning for transportation and refining. And the commodity specialist may study the petroleum's nonhydrocarbon components to seek potential new sources of valuable commodities.

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Natural Gas

By Keith A. Kvenvolden[1]

The principal hydrocarbon component in natural gas is methane, and a common diluent of this methane is nitrogen. These two components of natural gas are the focus of this discussion, the purpose of which is (1) to describe briefly the current thinking about their origins, (2) to redefine terms associated with the origin of methane, and (3) to suggest possible implications with regard to exploration strategies.

It is now widely recognized that methane in natural gas has multiple origins (Schoell, 1988). Most methane in natural gas has the same ultimate source, namely biologically formed organic matter. The reason that methane is said to have multiple origins is that a variety of processes act on this organic matter at varying levels of intensity.

Methane is predominantly a product of the conversion of organic matter by both biochemical (microbial) and thermochemical reactions taking place in different temperature regions. Methane that is ultimately derived from organic matter should be termed biogenic as opposed to abiogenic methane, which forms by chemical processes that do not involve organic matter. This definition of biogenic methane is different from that which has been commonly used, for example, by Schoell (1980, 1983) and Rice and Claypool (1981). In the past, the term biogenic described methane formed by microbial processes; in the future, this gas should be referred to as microbial (bacterial) methane (Jenden and Kaplan, 1986; Coleman and others, 1988). That methane which results from the thermochemical conversion of organic matter is a kind of biogenic gas that should continue to be called thermogenic methane, and methane produced by this process forms about 80 percent of the commercial deposits of natural gas; the remaining 20 percent of commercial deposits contain microbial gas (Rice and Claypool, 1981).

The various processes which lead to the formation of methane can often be differentiated by means of carbon and hydrogen isotopic compositions (fig. 5). For example, the formation of microbial methane follows two principal pathways: CO_2 reduction and fermentation (Jenden and Kaplan, 1986; Martens and others, 1986; Whiticar and others, 1986; Burke and others, 1988). Fermentation-derived methane is characterized by its depletion in the heavier isotope of hydrogen, that is, deuterium (fig. 5). The methanogenic pathways can operate simultaneously but are quantitatively important at different stages of sediment deposition. The pathways are generally independent of depositional environment but can be seasonally controlled. The fermentation processes are quantitatively more important in recently deposited sediments and swamps, whereas CO_2-reduction processes are more common in older sediments; microbial methane in commercial gas fields usually is the product of the CO_2-reduction pathway. Temperature, organic substrate, and age may be the major factors controlling the relative importance of the two pathways (Schoell, 1988).

Thermogenic methane is found in a wide variety of geologic settings and sedimentary basins, and it has a wide range of isotopic compositions (fig. 5), with oil-associated methane having generally more negative isotopic values and non-associated methane having more positive values. These isotopic compositions seem to be controlled by the geologic history of the basins and include such factors as the extent of conversion of organic matter and the timing of gas expulsion, migration, and trapping (Schoell, 1988). Isotopic compositions of thermogenic (oil-associated) methane partially overlap the isotopic compositions of microbial methane. Nevertheless, the isotopic compositions of methane provide an invaluable tool for differentiating among various processes involved in methane formation and occurrence.

Abiogenic methane is thought to form by inorganic chemical processes. Methane emanating from midocean-ridge hydrothermal systems is considered to be abiogenic and is characterized by heavy (more positive) carbon and hydrogen isotopic compositions (fig. 5). Abiogenic methane is a rather exotic form of methane (Schoell, 1988) and has not been shown to be commercially important.

Nitrogen is one of many nonhydrocarbon components of natural gas, ranging from trace amounts to concentrations approaching 100 percent (U.S. Bureau of Mines, 1983). The possible sources of nitrogen include (1) thermal degradation of organic matter in sediments, (2) maturation of coal beds, (3) diffusion from igneous and metamorphic rocks, and (4) trapped air (Hunt, 1979). The origin of nitrogen-rich natural gas is still puzzling. In a recent study of this kind of gas in the Sacramento basin of California, Jenden and others (1988) concluded that the gas is derived from metasedimentary rocks of the Franciscan complex thrust beneath the Great Valley during late Mesozoic and early Cenozoic convergence. In reaching this conclusion, they point

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out two factors of importance to natural gas exploration. First, the use of nitrogen isotopic compositions, at least in the Sacramento basin, is not very diagnostic and does not permit a satisfactory distinction between sedimentary, low-grade metasedimentary, and igneous sources. Second, hydrocarbon-rich and nitrogen-rich gases in this basin are genetically unrelated; thus the occurrence of nitrogen should not necessarily be used to predict the presence of nearby hydrocarbon accumulations, as was previously recommended (Getz, 1977).

In summary, this discussion has demonstrated the utility of carbon and hydrogen isotopes of methane to help decipher the processes that produced the methane. This information can be useful in developing strategies for further exploration. In contrast, the nitrogen isotopic composition of nitrogen in natural gas does not appear to be particularly diagnostic, and the origin of nitrogen-rich natural gas is generally not well understood.

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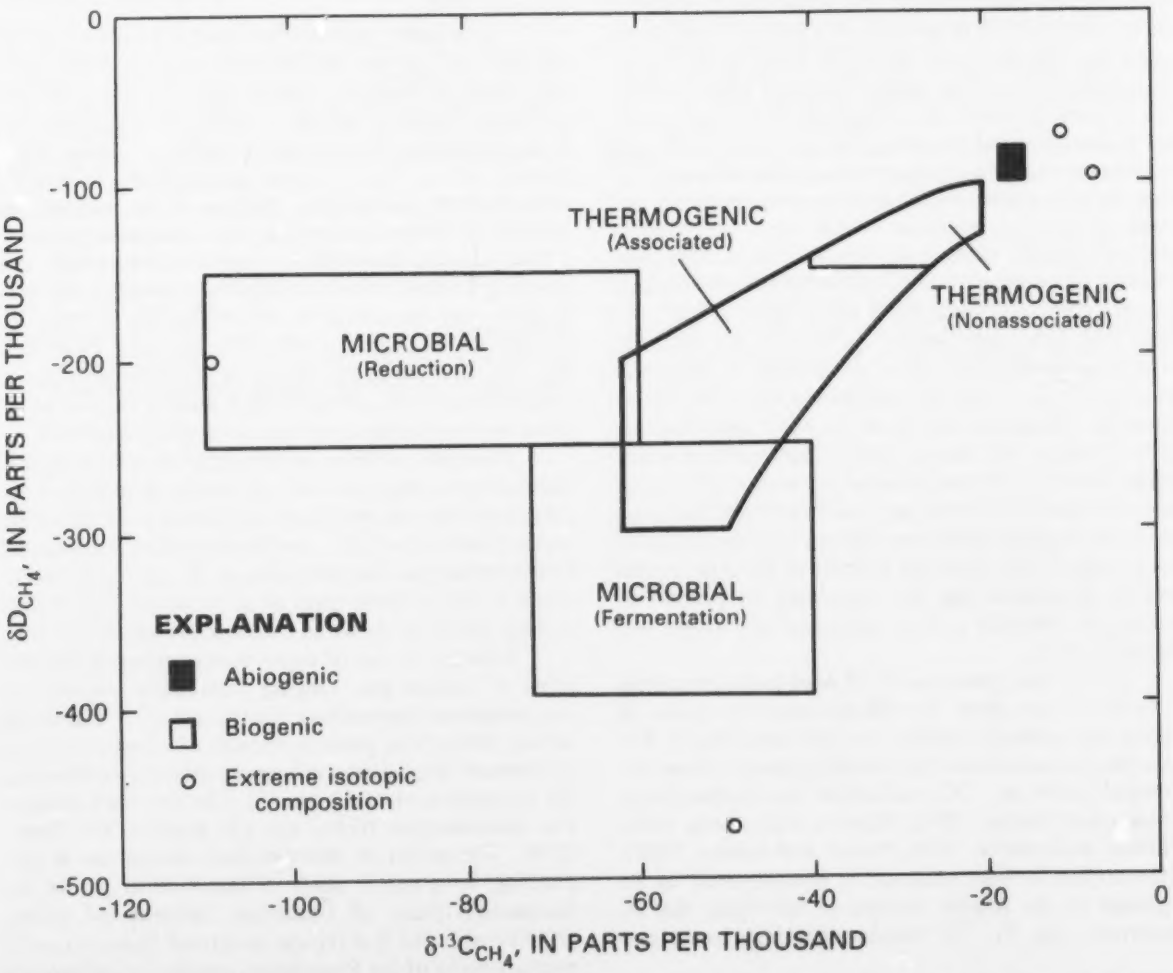

Figure 5. Carbon and hydrogen (deuterium) isotopic compositions in naturally occurring methane (modified from Schoell, 1988).

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Natural Gas Hydrates

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Gas hydrates are crystalline substances composed of water and gas in which a solid-water lattice accommodates gas molecules in a cagelike structure. In gas hydrates, water crystallizes in the cubic crystallographic system, forming structure I or II geometries depending on the composition of the gas; structure I gas hydrate is more commonly expected in nature (Davidson and others, 1978). Molecules of gases such as methane and ethane are small enough to be included in the water lattice of a structure I gas hydrate. At standard conditions (STP), one volume of structure I methane hydrate may contain as much as 164 volumes of methane gas (Davidson and others, 1978); because of this large volumetric conversion gas hydrates may represent an important source of natural gas.

Gas hydrates occur in sedimentary deposits under conditions of pressure and temperature that are present in permafrost regions and beneath the sea in outer continental margins (reviewed by Kvenvolden and McMenamin, 1980). Geologic, geochemical, and geophysical evidence of gas hydrates in both the marine and permafrost environments include (1) high concentrations of methane in sedimentary deposits, (2) gas released from cores in the amounts expected for decomposing gas hydrate, (3) seismic anomalies that can be explained by the properties of sediments containing hydrates, and (4) geophysical well-log responses indicative of hydrate-bearing sediments.

The presence of gas hydrates in offshore continental margins has been inferred mainly from anomalous seismic reflectors that coincide with the predicted transition boundary at the base of the gas-hydrate stability zone. This reflector is commonly called a bottom-simulating reflector or BSR. BSR's have been mapped at depths below the sea floor ranging from about 100 to about 1,100 m (Kvenvolden and McMenamin, 1980). The trapped free gas associated with BSR's represents a drilling hazard, and as such they have never been knowingly drilled; thus, BSR's are not proven to be caused by hydrates. However, gas hydrate samples recovered from wells drilled near BSR's indirectly confirm that BSR's are the consequence of gas hydrates. Gas hydrates have been recovered within 6.5 m of the sea floor in sediment of the Black Sea (Yefremova and Zhizhchenko, 1975) and the Gulf of Mexico (Brooks and others, 1986). Also, gas hydrates have been recovered at greater subbottom depths during research drilling and coring off the southeastern U.S.A. (Kvenvolden and Barnard, 1983), Mexico (Shipley and Didyk, 1982), Guatemala (Harrison and Curiale, 1982; Kvenvolden and MacDonald, 1985), and Peru (Kvenvolden and Kastner, 1989).

Cold surface temperatures at high latitudes are conducive to the development of onshore permafrost and gas hydrate in the subsurface. Gas hydrates are known to be present in the western Siberian platform (Makogon and others, 1972) and are believed to occur in other permafrost areas of northern USSR, including the Timan-Pechora province, the eastern Siberian craton, and the northeastern Siberian and Kamchatka areas (Cherskiy and others, 1985). Permafrost-associated gas hydrates are also present in the North American Arctic. Well-log responses, attributed to the presence of gas hydrates, have been obtained in about a fifth of the wells drilled in the Mackenzie Delta, and in the Arctic Islands over half of the wells are inferred to contain gas hydrates (Judge, 1988). On the North Slope of Alaska gas hydrates have been identified in 34 petroleum industry wells using geophysical well-log responses calibrated to the response of an interval in one well where gas hydrates were recovered in a core by ARCO and Exxon (Collett and others, 1988). Most of the North Slope gas hydrates occur in a series of laterally continuous Upper Cretaceous and lower Tertiary sandstone and conglomerate rock units, all geographically restricted to the area overlying the eastern part of the Kuparuk River oil field and the western part of the Prudhoe Bay oil field. Preliminary resource calculations suggest that the volume of gas within these hydrates is approximately 8 to 10 trillion cubic feet. Geochemical analyses of well samples from the Prudhoe Bay-Kuparuk River area suggest that the gas hydrates consist of a mixture of microbial and thermogenic gas. It is postulated that the thermogenic gas migrated from deeper reservoirs along the same faults thought to be migration pathways for the large volumes of heavy oil that occur at shallow depths in this area. The combined information from Arctic gas-hydrate studies shows that in permafrost regions, gas hydrates may exist at subsurface depths ranging from about 130 to about 2,000 m. Gas hydrates may also be associated with permafrost in Antarctica, but few data are available (Hitchon, 1974; MacDonald, 1983); land-temperature profiles suggest that gas hydrates could exist to depths as great as 2,000 m.

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Because large quantities of gas hydrates are widespread in permafrost regions and in offshore marine sediments, they may be a potential energy resource. Estimates of the amount of gas in hydrates of oceanic and continental settings range from 1.2×10^5 to 2.7×10^8 trillion cubic feet (adapted from Potential Gas Committee, 1981). With such a large resource potential, numerous recovery schemes have been suggested. As reviewed by Yousif and others (1988), the three most practical schemes for the production of gas from hydrates are (1) thermal stimulation, in which an external heat source is used to dissociate the hydrates, (2) depressurization, in which the production of associated free gas lowers reservoir pressures to cause decomposition of the hydrates, and (3) the use of gas hydrate inhibitors, in which a substance such as methanol is used to disequilibrate the hydrate. The Soviets have used the depressurization scheme to demonstrate that hydrates are an immediate, producible source of natural gas; their Messoyakha gas field in the West Siberian basin produced about 70 billion cubic feet of gas from hydrates over an eight-year period (Y.F. Makogon, Ministry of Gas Industry, Moscow, written communication).

Recent drilling and geologic sampling on the North Slope of Alaska have revealed the presence of a gas hydrate/free gas contact at the predicted base of the methane-hydrate stability zone, and a similar contact has been noted at the Russian Messoyakha hydrate gas accumulation. Future work on the North Slope will focus on the relation between the gas hydrate and associated free-gas accumulations. An assessment will be made of the production characteristics and economic potential of both the hydrates and related free-gas occurrences.

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Quantitative Petroleum Resource Assessment Methodologies

By Robert A. Crovelli[1]

INTRODUCTION

The geologic appraisal model that is selected for doing a petroleum resource assessment depends upon the purpose of the assessment, the basic geologic assumptions of the area, the type of available data, the time to deadlines, the human and financial resources, the available computer facilities, and, most important, the existing quantitative methodology with corresponding computer software and any new quantitative methodology that would have to be developed. Therefore, different resource assessment projects usually require different geologic models. Also, more than one geologic model might be needed in a single project for assessing different regions of the study area or for crosschecking the resource estimates of the study area. Some geologic analyses used in the past for petroleum resource appraisal involved play analysis. The corresponding quantitative methodologies of these analyses usually consisted of Monte Carlo simulation techniques.

The U.S. Geological Survey's petroleum resource appraisal studies have resulted in a wide variety of analyses, geologic models, quantitative methods, and computer programs. The type of analysis refers to the basic geologic assessment unit; for example, province, basin, or play. The geologic model consists of the geologic assumptions and mathematical description of the assessment approach; for example, reservoir engineering, volumetric yield, field size, or direct assessment. The quantitative method is the type of probabilistic methodology that is mathematically derived from the geologic model; for example, Monte Carlo simulation or analytic probability theory. The computer software is written on the basis of the probabilistic methodology.

PAST METHODOLOGIES

Some past petroleum resource appraisal studies by the U.S. Geological Survey are as follows.

1. The United States study (Miller and others, 1975) assessed the petroleum provinces in the United States using a direct-assessment model, a volumetric-yield submodel, and a Monte Carlo method for estimates of aggregations with the computer program called MIT: Massachusetts Institute of Technology.

2. The National Petroleum Reserve in Alaska (NPRA) study (U.S. Department of the Interior, 1979; White, 1981) assessed geologic plays in the North Slope of Alaska using a reservoir-engineering model and a Monte Carlo method with the computer program RASP: Resource Appraisal Simulation for Petroleum.

3. The Arctic National Wildlife Refuge (ANWR), which was formerly called the William O. Douglas Arctic Wildlife Range (Mast and others, 1980), was assessed in a similar manner as the NPRA study.

4. The United States study (Dolton and others, 1981; Crovelli, 1981, 1984a) was conducted in a similar manner as the 1975 United States assessment; however, an analytic probabilistic methodology was developed for individual province estimates and resulted in the computer package NASP: National Appraisal System for Petroleum.

5. The Devonian shale study (Charpentier and others, 1982) was an assessment of unconventional natural-gas resources in the Devonian shale of the Appalachian basin; play analysis was applied using a reservoir- engineering model and a Monte Carlo method with the computer program MRASP, a modified version of RASP.

6. The world oil study (Masters and others, 1983; Crovelli, 1984b, 1985a) assessed the oil basins in the world using basically the same approach as the 1981 United States assessment; however, an analytic probabilistic methodology was also developed for aggregating the basin estimates and resulted in the computer package WASP: World Appraisal System for Petroleum.

7. The Wilderness Lands in the Western United States study (Crovelli, 1983, 1984c, 1985b, 1986; Crovelli and Balay, 1984) assessed geologic clusters using a direct-assessment model, a richness-factor submodel, and an analytic probabilistic methodology for individual cluster estimates and aggregations with the computer package WLASP: Wilderness Lands Appraisal System for Petroleum.

8. The world oil and gas study (Masters and others, 1987) assessed the oil and gas basins in the world using basically the same approach as the 1983 world assessment; however, a completely analytic probabilistic methodology was developed and resulted in the revised computer package RWASP: Revised World Appraisal System for Petroleum.

[1]U.S. Geological Survey, Denver, Colo.

PRESENT METHODOLOGIES

During recent years, the U.S. Geological Survey has made major strides to design and develop petroleum resource appraisal studies involving play analysis and analytic probabilistic methodology with a variety of geologic models. Play analysis is a general approach using various geologic models and probabilistic methods for analyzing a geologic play. In applying play analysis, a petroleum assessment area is first partitioned into geologic plays, and then the individual plays are analyzed. The individual play estimates of oil and gas are aggregated, respectively, in order to estimate the petroleum potential of the entire assessment area.

A probabilistic system of petroleum resource appraisal for play analysis has been designed to meet the following requirements: (1) includes a variety of geologic models, (2) uses an analytic methodology instead of Monte Carlo simulation, (3) possesses the capacity to aggregate estimates from many areas that have been assessed by different geologic models, and (4) runs quickly on a microcomputer. The geologic models for play analysis consist of four basic types: reservoir engineering, volumetric yield, field size, and direct assessment. The order in which the models are listed reflects the decreasing amount of geologic information that is required in the model.

The reservoir-engineering model is the most data-intensive model and was used in the three recent petroleum resource appraisal studies by the USGS given below. These three assessments are followed by studies using less data-intensive models.

1987 Arctic National Wildlife Refuge Assessment

The Arctic National Wildlife Refuge (ANWR) study (Crovelli and Balay, 1986; Crovelli, 1987a, 1987b, 1988; Dolton and others, 1987) assessed in-place oil and gas resources of geologic plays in the North Slope of Alaska using a reservoir-engineering model. The model is similar to the reservoir-engineering model in the 1980 ANWR assessment except that some of the parameter values in the reservoir-engineering equations were changed.

An analytic probabilistic methodology using probability theory was developed for play analysis in the 1987 ANWR study based upon the reservoir-engineering model. A computer software package consisting of six computer programs was created and called Fast Appraisal System for Petroleum, Reservoir Engineering (FASPRE). Some of the details of the analytic method and the computer package FASPRE were presented by Crovelli and Balay (1986).

Hungary Assessment

The Hungary assessment of the Békés basin involved generalizing the reservoir-engineering model and the aggregation model that were used in the 1987 ANWR study (Crovelli and Balay, in press). The modifications included the requirements that the system produce output in metric units and run on an IBM-PC-XT compatible computer. A user's manual was also written that included guides for installation and operation of the system.

The purpose of modifying the existing reservoir-engineering model was to make the geologic model universal and, therefore, applicable anywhere in the world. This was necessary since the model in the 1987 ANWR study was site-specific, being only applicable in the North Slope of Alaska.

The analytic probabilistic methodology was derived from the methodology for the 1987 ANWR study by replacing the site-specific reservoir-engineering equations with a new general system of equations and parameters. Therefore, through extensive modification of the FASPRE package, the universal metric version of the play analysis computer software package was built and called FASPUM. The FASPUM software is available to the general public through the Open-File services of the USGS (Crovelli and Balay, 1987).

Tight Gas Sands Assessment

The Tight Gas Sands study (Johnson and others, 1987) is an assessment of low-permeability gas resources of the Upper Cretaceous Mesaverde Group in the Piceance basin of western Colorado. The resource appraisal system used in this study was derived from the generalized system of the universal metric study and the 1987 ANWR study. Modifications were made that included conversion to U.S. Customary units. The computer software package FASPUE is essentially the U.S. version of the metric version FASPUM. Therefore, FASPUE is a universal U.S.-units, play-analysis system using a reservoir-engineering model and an analytic probabilistic methodology. The FASPUE software is available to the general public (Crovelli and Balay, 1988, 1989).

The ANWR study was designed to assess conventional oil and gas accumulations which are treated as a set of prospects in a play area. However, the Tight Gas Sands study is an assessment of unconventional low-permeability gas reservoirs. Therefore, an entire play area is treated as a single gas accumulation. The hydrocarbon reservoir parameters are also assigned accordingly. The mathematical formulation of the geologic model is appropriate for conventional and unconventional petroleum resources. The different applications require different physical interpretations of the geologic model.

Federal Offshore Assessments

The Minerals Management Service (MMS), an agency of the U.S. Department of the Interior, made a systematic assessment of the undiscovered economically recoverable oil and gas resources for Federal offshore areas (Cooke, 1985). The MMS study of Federal offshore areas applied a prospect analysis using a volumetric-yield model and a Monte Carlo method with the computer program PRESTO.

The Bureau of Land Management (BLM), an agency of the U.S. Department of the Interior, made the assessment of the undiscovered economically recoverable oil and gas resources for the 1987 ANWR study. The BLM assessment utilized the PRESTO program. The USGS was responsible for making the in-place assessment, while the BLM was responsible for the recoverable assessment in the 1987 ANWR study.

The volumetric-yield model is not as data-intensive as the reservoir-engineering model; that is, not as many hydrocarbon-volume attributes are involved. Some of the hydrocarbon-volume attributes in the reservoir engineering equations are combined into a single factor, called the oil yield factor in the oil volume equation and the gas yield factor in the gas volume equation. Estimates of oil and gas yield factors as distributions indicate the amount of hydrocarbons expected per volume of reservoir rock (acre-foot).

National Assessment

The USGS recently completed its first petroleum resource appraisal of the entire United States using play analysis (Mast and others, 1989). The major geologic model in the play analysis is the field-size model. A probability model incorporating the field-size distributions of oil and gas was designed with a risk structure that is quite different from FASPRE and FASPUE.

An analytic probabilistic methodology was developed for play analysis in the United States study based upon the field-size model and the new risk structure. A computer software package consisting of 11 computer programs was written and called Fast Appraisal System for Petroleum, Field Size (FASPF).

The field-size model is based upon an assessment of the size of the fields in the play and not the individual geologic hydrocarbon-volume attributes. The volumes of oil and gas accumulations are modeled as statistical distributions in the form of histograms or probability distributions. Field-size distributions are used two ways: (1) the distribution is of known fields from an explored area, and the distribution is used to estimate the resources of the remaining fields in that area, and (2) the distribution is used as an analog in geologically similar unexplored areas (Houghton, 1988).

A summary of the past and present petroleum resource appraisal studies by the USGS discussed in this paper is presented in table 5.

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Table 5. Summary of some past and present petroleum resource assessments by the U.S. Geological Survey

Assessment	Year	Analysis	Model	Method	Software
United States	1975	Province	Direct assessment (volumetric yield)	Monte Carlo	MIT
NPRA[1]	1979	Play	Reservoir engineering	Monte Carlo	RASP
ANWR[2]	1980	Play	Reservoir engineering	Monte Carlo	RASP
United States	1981	Province	Direct assessment (volumetric yield)	Monte Carlo & Analytic	NASP
Devonian Shale[3]	1982	Play	Reservoir engineering	Monte Carlo	MRASP
World	1983	Basin	Direct assessment (volumetric yield)	Monte Carlo & Analytic	WASP
Wilderness Lands	1983	Cluster	Direct assessment (richness factor)	Analytic	WLASP
World	1987	Basin	Direct assessment (volumetric yield)	Analytic	RWASP
ANWR	1987	Play	Reservoir engineering	Analytic	FASPRE
Hungary	1987	Play	Reservoir engineering	Analytic	FASPUM
Tight gas sands	1987	Play	Reservoir engineering	Analytic	FASPUE
United States	1988	Play	Field size	Analytic	FASPF

[1]National Petroleum Reserve in Alaska.

[2]Arctic National Wildlife Refuge in Alaska.

[3]Devonian Shale of Appalachian basin.

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